The Thesis Committee for Nicholas John Kuzmyak
Certifies that this is the approved version of the following thesis:

Evaluation of Friction Reducers for Use in Recycled Fracturing Flowback and Produced Water

APPROVED BY
SUPERVISING COMMITTEE:

Co-Supervisors:

Lynn E. Katz

Eric van Oort

Evaluation of Friction Reducers for Use in Recycled Fracturing Flowback and Produced Water

by

Nicholas John Kuzmyak, B.S. Env. E.

Thesis

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science in Engineering

The University of Texas at Austin

May 2014

Acknowledgements

I am grateful to my advisors, Dr. Lynn Katz and Dr. Eric van Oort, for their guidance and mentoring, as well as the opportunity to work on this exciting research project. Thanks are in order to Dr. Mukul Sharma as well for inclusion in engaging research group meetings and for providing interesting perspectives on the research.

The research groups of Drs. Katz, Van Oort, and Sharma have been continuous sources of support for various lab troubleshooting sessions, and general experimental knowledge. In particular, my colleague Arielle Mimouni has been instrumental in the completion of this work, and significantly aided me in flow loop design and construction, the majority of cloud point testing, and presentation preparations.

Various members of the school of Petroleum and Geosystems Engineering (PGE) have been indispensable for this research project. I would like to specially thank Rod Russell for help with a large amount of apparatus construction and graciously lending the physical space, tools, and patience that were often needed for the flow loop experiments. Daryl Nygaard of PGE was responsible for much of the custom fabrications on the flow loops, as well as their design, construction, and material sourcing; much appreciation is in order there. Thanks as well go to Glen Baum, who has been an excellent and patient consultant and constructor for all things lab and facility related, and to Tesse Smitherman for making absolutely sure that the project had the supplies it needed as soon as possible. Finally, Michelle Shuck was instrumental in acquainting me with working in a different department (PGE) as well as helping with various construction and sourcing challenges.

Throughout the research project, I have been fortunate to converse and consult with numerous industry professionals who have lent their considerable experience and

knowledge to this project. In particular, I would like to thank John Downs of Dow, Ron Powell of Trican Well Services, Marcelle Ferguson of Nalco Chemical, David Wright of SNF Inc., Zach Ritter of Liberty Process, and Charles Falgout of Pump Energy. Through providing samples, helping with troubleshooting specific equipment, and providing potential directions for the research to go, this network has been extremely helpful in furthering this project.

Finally, I am very grateful for the funding from Shell, the sponsor of this project, as well as the financial assistance provided by the University of Texas' Friends of Alec scholarship fund.

Abstract

Evaluation of Friction Reducers for Use in Recycled Fracturing and Produced Flowback Water

Nicholas John Kuzmyak, M.S.E.

The University of Texas at Austin, 2014

Supervisors: Lynn E. Katz, Eric van Oort

The continued expansion of hydraulic fracturing activity in North America – especially in slickwater operations – has given rise to concerns regarding water quantity and quality. On one hand, operators in arid areas must compete with other users to obtain enough fresh water to perform fracturing operations, while in other areas the flowback water after a treatment must be either expensively treated or disposed of in injection wells, which are in very limited supply in regions such as the Marcellus Shale. Reuse of these highly saline waters can help to alleviate both of these problems. However, water that contains concentrated and difficult-to-remove salt ions – especially divalent cations – cannot be used with typical polyacrylamide friction reducers, due to these additives' dramatically decreased effectiveness in such fluids. Otherwise, reuse would be an attractive option and, in fact, this practice is widespread in multiple US shale plays with the recent advent of salt-tolerant polyacrylamides.

This research attempts to quantify the effect of high salt concentrations on the effectiveness of friction reducers through construction of a flow loop apparatus that

allows for observation of turbulent drag reduction. The polymers tested were chosen from industry standards (inverse oil-emulsion salt-tolerant anionic polyacrylamide), novel polyacrylamides (highly salt-tolerant polyacrylamide dispersed in concentrated brine), and an overlooked yet potentially highly effective polymer (i.e. polyethylene oxides, PEOs). PEOs, in particular, have been known as highly efficient friction reducers in brines for over 50 years, but are not used in the fracturing industry for various reasons. These three additives were tested at concentrations of 0.1% in solutions of sodium chloride, calcium chloride, and a multisolute brine of both salts.

The experiments show that the typical salt-tolerant polyacrylamide is indeed negatively affected by the divalent calcium ions, while the novel polyacrylamide is a strong performer (up to 60% friction reduction) in even the strongest brines. Interestingly, the PEOs consistently produced about 45% friction reduction (based on the base fluid pipe friction pressure drop), and did so at low concentrations (<0.1%) for a range of molecular weights.

The major conclusion of this research is that even highly concentrated brine can be recycled with minimal treatment if either the novel polyacrylamide or PEOs are used, opening the door for potential use of other atypical brine sources in hydraulic fracturing operations. The PEOs are especially interesting because, though overlooked, they are economical, readily available, and salt-tolerant. Future experiments will be run on a larger flow loop to potentially optimize PEO characteristics and further demonstrate their viability as an alternative to polyacrylamides.

Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

In the United States, exploitation of shale gas and other unconventional hydrocarbon resources has greatly expanded over the past few years due to the combination of two recently improved oilfield technologies: horizontal drilling and hydraulic fracturing, often referred to as "fracking." This activity has enabled economical production of resources that were previously inaccessible, due to the ability of fracturing to expose large areas of low-permeability shale reservoirs and the possibility of contacting larger extents of shale beds afforded by horizontal drilling. The basic idea of hydraulic fracturing involves injecting a fluid – such as gel, acid, or water – into a hydrocarbon-bearing formation at high flow rates and high pressure, causing the rock to crack and form complex fracture networks. Once the fluid flows back from the subsurface, gas is free to flow out of the formation rock to surface production infrastructure. In the US, water with small concentrations of friction reducer – "slickwater" – is used to fracture tight gas formations with very low permeability (often shale, but formations with different mineralogy are also exploited)

The recent explosion in fracturing activity, juxtaposed with the US goal of energy independence and the environmental risks associated with fracturing, has garnered attention in academia, industry, and public media, leading to frequent debate regarding the risks versus gains. Economically, the development of shale gas reserves has proven fruitful for the US energy sector, keeping natural gas prices low while reducing dependence on hydrocarbon imports. It is estimated that there is as much recoverable gas in US tight shale reservoirs as the total amount of conventional gas discovered in the past 150 years. Industry experts have asserted that, if managed and regulated properly, the fracturing industry can allow the US to achieve greater energy independence and

economic security with minimal environmental risk (Howarth, Ingraffea, & Engelder, 2011).

Conversely, the environmental risks and challenges resulting from fracturing are myriad, and include air pollution (from both methane leaks and flaring, as well as truck traffic), habitat fragmentation, and many water-based issues: large volumes of high-salt content flowback and produced water (and difficulty of treatment/disposal), potential aquifer contamination from methane leaks in well casings, overflowing of surface impoundments that could affect ground and surface waters, and the large draws of fresh water necessary to undertake operations (Howarth, Ingraffea, & Engelder, 2011). As mentioned before, the vast majority of US fracturing uses slickwater, which consists of over 99.5% water and proppant by fluid volume (Jenkins, 2012). The remainder of the formulation is made up of chemical additives that aid in the fracturing operation by reducing pipe friction pressure, stabilizing clay in the formation, and inhibiting corrosion of the well casing.

1.1 WATER SCARCITY

Both water and energy are vital to a strong economy and functional society, but the uneven distribution of water over the world can contribute to shortages or even conflicts. Climate change is causing the distribution to be even more unpredictable, while both developed and developing countries grow economically and in population – projections indicate a 20 to 40 percent rise in domestic water demand, as well as 20 to 40 percent more demand for agriculture (Hightower, 2011). Meanwhile, water use for the energy industry is expected to increase by 30 to 100 percent globally. Clearly, water is in high demand and will become scarcer in the near future, and a water-intensive industry like fracturing will be affected.

In the US, both surface and groundwater are also distributed unevenly, and are generally decreasing. For illustration, Figure 1 shows the extent of groundwater depletion in the contiguous US, focusing on aquifers that have monitoring wells run by the United States Geological Survey (USGS). Note that, in the legend for aquifer health, "High" refers to the average well level being constant or increasing over the last few years, and "Low" indicates that sample wells are at decreased levels relative to the last few years. Aquifers in which well water levels have dramatically dropped would be considered in low health. As can be seen, many of the country's groundwater levels have dropped significantly.

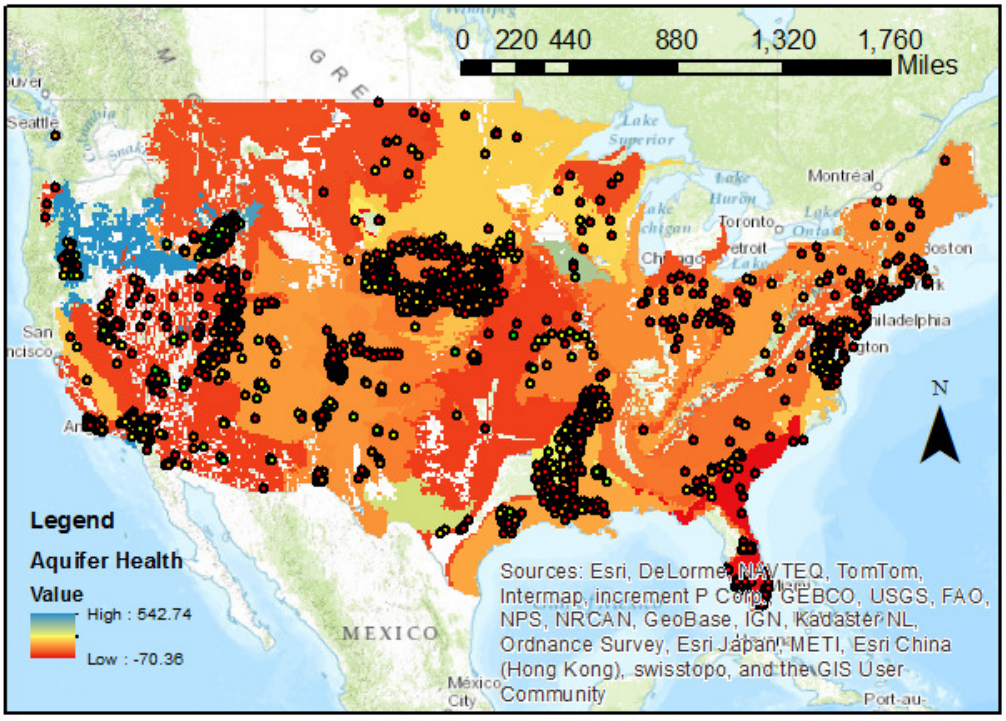

Figure 1 – Aquifer Depletion per USGS

One of the most pressing issues facing the fracturing industry is the dilemma of sourcing water for operations and treating or disposing of the water returned after

injection – termed flowback (includes mostly injected fluids) or produced (water included with the produced hydrocarbon) water (Horn, 2009). The former problem is encountered in shale plays located in arid regions of the US, where fresh water is scarce or there are competing interests. This is the case in formations such as the Eagle Ford, Barnett, and Bakken, where water use for fracturing must compete with agricultural, municipal, and industrial activities. The other water supply issue – treating or disposing of flowback and produced water – is an issue in formations such as the Marcellus Shale in the northeast US. Though decent water supplies are available, this region's historically minimal involvement in the petroleum industry means that there are few deep disposal wells or treatment plants equipped to handle the waste water. Frequently, the wastewater must be transported to areas with injections wells, often at great cost – up to $10 a barrel (Puder & Veil, 2007).

For many operators faced with the issue of contaminated flowback and produced water that cannot be easily disposed of, the most logical option is to simply treat and reuse the water. As of 2012, many oil and gas companies were reusing up to 90% of flowback water; however, it must be noted that only about 20 to 40% of the water pumped into the formations is returned post-injection (Jenkins, 2012). The options available for a company aiming to reuse flowback water are to either treat the water onsite or blend it with fresh water for reuse in subsequent operations. Unfortunately, onsite treatment is often expensive and requires specialized. Blending is also an undesirable option, since the contaminants returned with flowback water can detrimentally affect additives that must be used in fracturing operations, specifically friction reducers that are affected by salt ions. Water laden with ions such as Na^+, Ca^{2+}, and Cl^- can prevent conventional friction reducers – often polyacrylamides emulsified in an oil phase – from working properly. Without friction reduction, the enormous flow

rates needed to suspend proppant and fracture a shale formation cannot be achieved safely nor economically; the surface pressure required would simply be too high (Robb, Welton, Bryant, & Carter, 2010). With these problems to surmount, various researchers and chemical companies have sought to develop additives that will work with these brines, thus greatly simplifying flowback water reuse.

1.2 SUTUR PROJECT

The Shell/University of Texas Unconventional Resources (SUTUR) project comprises a number of research projects between the school of Petroleum and Geosystems Engineering (PGE) and the Jackson School of Geosciences, and is focused on developing knowledge for the challenge of sourcing, extracting, and producing from unconventional hydrocarbon-bearing formations. The project discussed within this thesis is a small part of this initiative, and is included within a collaboration between the PGE, the Environmental and Water Resources Engineering program (EWRE), and the Bureau of Economic Geology (BEG). This particular group is focused on the cycle of water used in hydraulic fracturing. A flow chart outlining this cycle is shown in Figure 2.

In the project section covered by the BEG, researchers are seeking to characterize the chemical makeup of water in contact with shale under heat and pressure. This research seeks to gather empirical data for potential geochemical modeling, as well as ascertain the factors which determine the makeup of flowback water. The other active research in this project deals with the compatibility of the proposed fracturing fluid formulations and various shales, using hot rolling oven (HRO) dispersion tests and fracture conductivity experiments (Mimouni, 2014).

Figure 2 - SUTUR Workflow Diagram

The focus of the project detailed in this thesis resides in the bottom part of Figure 2: testing friction reducer efficiency based on various potential shale leachates. This entails evaluating various friction reducers, both conventional and novel, with different brine types and concentrations in order to develop an understanding of the factors that have the greatest impact on friction reducer performance. To accomplish this, various combinations of friction reducers and base fluids were run in a flow loop.

1.3 Scope of Thesis

This thesis addresses a specific part of the industry-wide need to recycle flowback and produced brines in fracturing: the development of friction reduction additives that are effective over a wide range of salt concentrations. To this end, the friction reducing

efficiencies of three additives have been tested in a flow loop that has been designed and constructed as part of this project. We hypothesized that two novel polymers (the dispersion polymer friction reducer, DPFR, and polyethylene oxide, PEO) would be nearly non-responsive to dramatic changes in salt concentration and type, as well as perform reasonably well as shale stabilizers. Through this work, it is envisioned that less expensive, more environmentally friendly, more salt tolerant and multifunctional additives can be an option to hydraulic fracturing operators struggling with low quantities or qualities of water, as well as those in regions where access to high-grade salt-tolerant polyacrylamides is not guaranteed. In addressing a petroleum engineering problem, the results of this experimental work also imply a potential gain in environmental responsibility for the industry. By drawing less fresh water and requiring less treatment or disposal of flowback water, the water footprint of hydraulic fracturing can be lessened.

1.4 ORGANIZATION OF THESIS

Chapter 2: Literature Review of this thesis is a review of the literature surveyed for this project, including all relevant concepts: contaminants found in flowback and produced water, water treatment techniques available, the mechanism of friction reduction in turbulent flows, relevant polymer chemistry for both polyacrylamides and the novel polymer, and a brief introduction to shale stabilization.

In Chapter 3: Experimental Methods, the experimental design and methods are explained. The criteria for designing the flow loop are discussed, as well as an explanation of the experimental protocol.

The results of the flow loop experiments are detailed in Chapter 4: Results and Discussion. The analysis and ramifications of the data generated will be discussed,

especially with respect to what they mean for the future of friction reducer usage in the fracturing industry.

Chapter 5: Conclusions summarizes the results of the research and presents conclusions drawn from this work, explains limitations encountered in the experiments, and suggests further research to be conducted.

Chapter 2: Literature Review

2.1 Overview

As mentioned in Chapter 1: Introduction, energy extraction is quite water intensive, both in the amount of freshwater required and the disposal needs for produced and flowback water. Hydraulic fracturing, in particular, is considered to be a major contributor to water stress in active regions, though often this stress is locally concentrated. For example, even in a relatively sparsely populated and active fracturing area like Alberta, Canada, the province-wide use of water for the entire petroleum industry is only 6% of the total water use (Paktinat, O'Neil, & Tulissi, 2011c). In fact, in the state of Texas, switching to unconventional natural gas for power generation would actually be a net water savings of about 60% (on the basis of gallon per kilowatt-hour), largely due to the higher efficiency of natural gas power plants and the water-intensive extraction of Texas lignite, which takes over seven times the gal/kWh that hydraulic fracturing consumes (Grubert, Beach, & Webber, 2012). Regardless of the big picture, however, obtaining freshwater and disposing of flowback water has been difficult enough for operators that many have been treating, recycling, and blending flowback since at least 2007 (Blauch, 2010). However, very little of the injected volume is returned from shale formations – typical values range from 20-40% (Howarth, Ingraffea, & Engelder, 2011; Jenkins, 2012) – and what does return is highly variable. Flowback water composition is generally similar to what is injected, but produced water varies widely between formations, and depending on the cumulative volume flowed back (Jenkins, 2012).

2.2 WATER ANALYSIS AND TREATMENT

Formation geochemistry is the most important determinant of the quality of produced water, though many researchers maintained that the mixing of fracturing fluid with formation brines was the major factor in determining salt concentration. This is now known to be false; ion exchange and leaching of minerals from the shale has been found to be the predominant cause of the high salt content (Blauch, Myers, Moore, & Lipinski, 2009). The wide variation in water quality is due to the heterogeneity of shale within individual plays and between regions. As an example, Table 1 presents the ranges of ionic species in a set of 5-day flowback water samples from 14 wells in the Marcellus Shale. Similar research shows that even between nearby shale plays, ion concentrations can be different by an order of magnitude or more (Paktinat, O'Neil, & Tulissi, 2011c). Though the concentrations of salt ions are quite high, heavy metal concentrations are actually orders of magnitude less than in typical municipal wastewater sludge (Hayes, 2011). In addition to the spatial variability in produced water quality, the ionic content also varies greatly with time, as can be seen in Figure 3.

Table 1 - Range of Ion Concentrations for Marcellus Shale 5-Day Flowback Samples (Hayes, 2011)

Ion	**Range (mg/L)**
Na^+	10,700-65,100
Ca^{2+}	1,440-23,500
Mg^{2+}	135-1,550
Fe^{2+}	10.8-180
Ba^{2+}	21.4-13900
Cl^-	26,400-148,000
HCO_3^-	29.8-162
NH_4^+	15-242

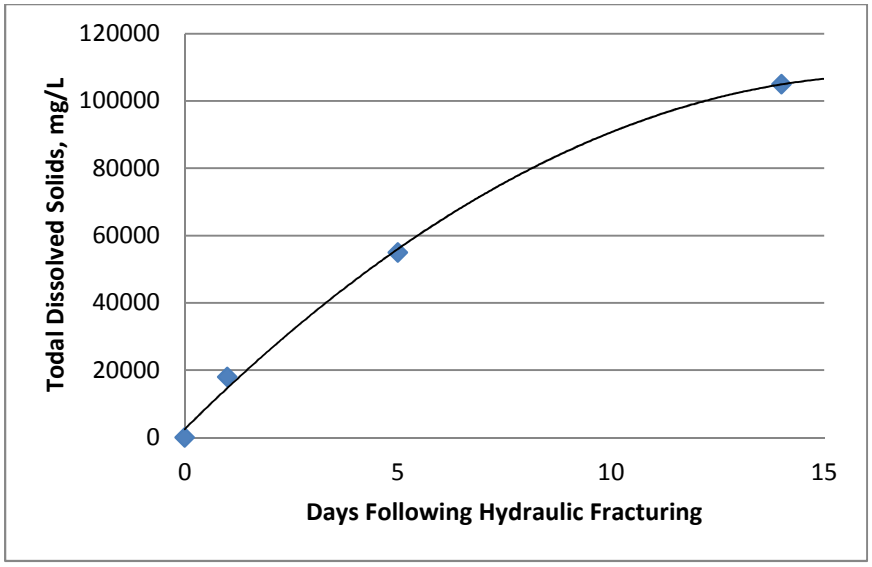

Figure 3 - Change in Produced Water Composition in Marcellus Shale Sample, Adapted from Hayes (2011)

Though the main contaminants of interest are salt ions in high concentrations (which cause the most interference with friction reducers), recycled water can also contain a variety of contaminants of concern including residual biocides (Aften, Paktinat, & O'Neil, 2011), enzymes of bacterial origin (Li, et al., 2010) and myriad organic compounds, of both natural and anthropogenic origin (Hayes, 2011). Of the salt ions, divalent species are the most problematic for friction reduction (Paktinat, O'Neil, & Tulissi, 2011b; Horn, 2009). Operators who recycle flowback and produced water have the option of contracting an established third party for onsite treatment (Hayes, 2011), blending with fresh water, determining the proper additives for reuse of the water through chemical analysis (Rimassa, Howard, & Blow, 2009), or even adding complexing agents to allow the polymer to work more effectively (Robb, Welton, Bryant, & Carter, 2010). Most treatment companies use thermal processing and/or membrane filtration, but new treatment techniques are being developed as well. For example, the utilization of advanced oxidation processes (AOPs) for destruction of volatile organics has been

instrumental in reducing fouling of reverse osmosis (RO) membranes in subsequent treatment processes (Horn, 2009). Despite the proliferation of treatment techniques and the contractors who employ them, it is operationally simpler to directly reuse water with as little onsite treatment as possible. However, this approach necessitates the use of salt-tolerant friction reducers, since the most important deleterious interaction is between the friction reducers and the ions in the flowback water (Papso, Blauch, & Grottenthaler, 2010). The friction reducers are absolutely necessary for the high-volume and high-rate nature of slickwater operations, and any water that has contacted a shale formation will leach out high concentrations of mono- and divalent ions that can affect these additives.

The rapid growth of the hydraulic fracturing industry in the US has been made possible partly by the improvement of friction reducers that allow slickwater-style treatments to be performed. Due to the higher cost of the additives required for a conventional gel-based fracturing operation, the need for a less viscous fluid to optimize the complex network of fractures desired in shale formations, and the potential for gel residue from traditional fluids, slickwater allows for a much reduced use of additives and per-volume fluid costs (Schein, 2005). However, since there are no solely viscosifying agents used in these operations (such as guar gum), high flow rates are necessary to prevent proppant from settling out of solution – often around 100 barrels per minute (bpm). At these very high flow rates, surface pressure due to pipe friction increases dramatically. For example – and as a rough estimate using the Darcy-Weisbach equation for a Newtonian fluid – given a typical pipe inner diameter for well tubing of 2.5”, a flow rate of 100 bpm, and typical parameters for fresh water (specific gravity of 1.0 and dynamic viscosity of 1 cp), the rise in pressure due to pipe friction is shown in

Figure 4. Though this is for the basic case where all pressure is due to pipe friction (not true in reality), it is clear that the application of a polymer that gives an average of 75% friction

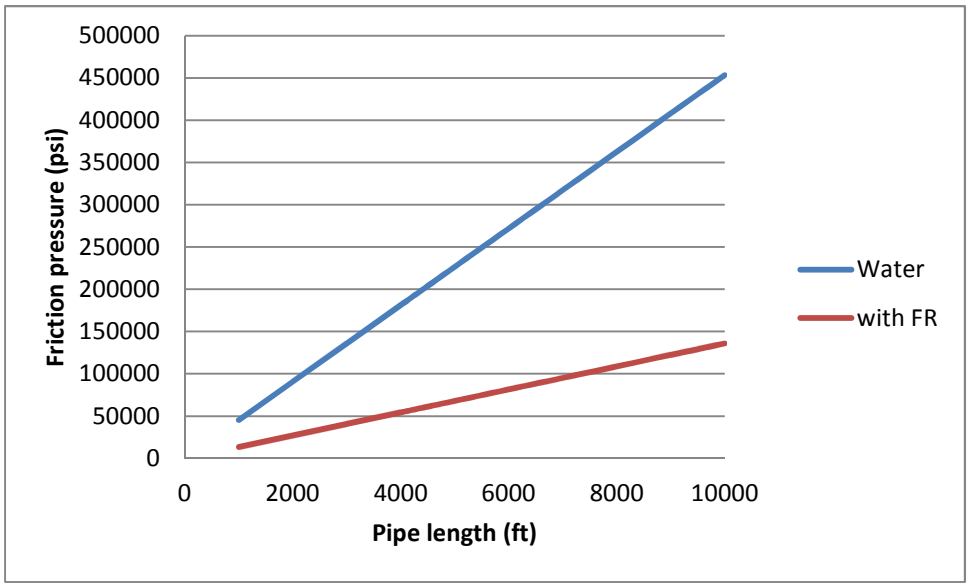

Figure 4 – Example Illustrating the Importance of Adding Friction Reducer, Assuming 75% Average Friction Reduction Percentage. Parameters are pipe inner diameter of 2.5", specific gravity of 1.0, and dynamic viscosity of 1 cp.

reduction would be quite advantageous for safety, reduced cost, and decreased demand on equipment. In coiled tubing operations – equipment through which fracturing is occasionally performed – pipe friction can even be up to 200% higher than in straight pipes (Lindsay, McNeil, Sackash, & Bryant, 2011). Therefore, the main purpose of friction reducers is to reduce surface pressure enough to allow fracturing with high flow rates of water – without these additives, shale gas fracturing would not be possible as it is today. Before describing specific friction reducer research, it is advantageous to understand the phenomenon of friction reduction from a theoretical standpoint in order to

fully appreciate the factors that make particular additives better than others or more resistant to decreased performance in saline waters.

2.3 RHEOLOGY

Turbulent drag reduction is the physical phenomenon of reducing skin friction in turbulent flow via additives (Virk, 1975). Since the first recognitions of this phenomenon in paper pulp transport in the 1930s (Shenoy, 1984), in flamethrower usage during World War II (Savins, 1964), and in the first experiments using a polymer dissolved in monochlorobenzene (Toms, 1948), the concept has garnered much attention in many fields including petroleum and civil engineering, naval hydrodynamics, agriculture, and medicine. Much research was done for naval institutions to reduce the drag around ships and submarines (Hoyt, 1972) – in fact, it was discovered that certain species of marine organisms have evolved the ability to secrete polymers to reduce drag around them (Hoyt & Fabula, 1964). Apart from hydrodynamics and pipe hydraulics, applications of friction reducers were envisioned for the treatment of arteriosclerosis by reducing blood friction (Shenoy, 1984), and current uses ranging from decreasing evaporative losses from spray irrigation (Dow Chemical Company, 2002) to increased fire hose spray distance (Sellin, Hoyt, Poliert, & Scrivener, 1982). Though empirical correlations were fairly straightforward to obtain through early flow experiments (both once-through and in loops), researchers struggled and debated over how to properly model the phenomenon, and a satisfactory "universal model" was not agreed upon for nearly four decades.

Though many different models were put forth by the hydrodynamics research community, a few considerations were included in most of the approaches. First, it was clear that for these types of solutions, drag reduction was not omnipresent, but a minimum trigger of turbulence must be achieved first; for example, a minimum Reynolds

number (Den Toonder, Hulsen, Kuiken, & Nieuwstadt, 1997) or the product $Re*f^{1/2}$ (Virk, 1975). One of the leading figures in the investigation of drag reduction, T.S. Virk, noted that a critical wall shear stress must be achieved in order for the solution to start showing friction reduction compared to the pure solvent (1975). This value is apparently independent of pipe diameter and polymer concentration, but increases with the size of randomly coiling polymers – that is, their radius of gyration. As an example of the disagreement characteristic of the investigation of this phenomenon, some researchers have implied that the onset of drag reduction is dependent on pipe diameter, since polymer molecules would be acting on the boundary layer, which would be proportionally larger as pipe diameter decreases (Hoyt, 1972). In addition to a minimum level of turbulence required for drag reduction to occur, there also exists a maximum asymptotic friction reduction efficiency that is independent of polymer type, pipe size, and Reynolds number, molecular weight, and concentration – this maximum is theoretically possible for any friction reducer (Hoyt & Fabula, 1964; Hoyt, 1972; Virk, 1975; Wang, Yu, Zakin, & Shi, 2011; Shenoy, 1984). This asymptote – via Virk – is as follows (1971):

$$\frac{1}{f^{1/2}} = 19.0 * \log_{10}\left(Re * f^{1/2}\right) - 32.4 \qquad \text{Eq 1}$$

compared to the condition of no drag reduction:

$$\frac{1}{f^{1/2}} = 4.0 * \log_{10}\left(Re * f^{1/2}\right) - 0.4 \qquad \text{Eq 2}$$

where f is the friction factor (unitless) and Re is the Reynolds number (unitless). Note that other drag reduction asymptotes have been put forth, such as the following from Wang et al (2011):

$$C_f = 1.4Re^{-2/3} \quad \text{Eq 3}$$

where C_f is the coefficient of friction, equivalent to the friction factor.

The profile of this modified pipe flow – which normally consists of a viscous boundary layer and a central turbulent zone – also produced considerable disagreement. Though early researchers postulated that friction reduction occurs due to thickening of the viscous boundary layer (Hoyt, 1972; Savins, 1964; Walsh, 1967; Van Driest, 1970), Virk's model included a third layer between these two – the elastic sublayer – to account for the elastic behavior of the solution in addition to its viscous properties (1971; 1975). As researchers found that the rate of turbulent eddy formation is on the same order of magnitude as the relaxation rate of randomly coiled polymers (Savins, 1964; Virk, 1971; 1975), most models are based on the assumption that the polymers must be responsible for either absorbing (Walsh, 1967; Savins, 1964) or dispersing the energy created by turbulent eddies (Gordon, 1970; Den Toonder, Hulsen, Kuiken, & Nieuwstadt, 1997). To account for absorption of turbulent eddy energy by polymer molecules, most models conceptualized the solution as consisting of discrete macromolecules with negligible interaction – a common agreement was that the solutions were too dilute to experience any effects from a "mesh" of polymer molecules (Savins, 1966; Paterson & Abernathy, 1970). Though many of the early models were able to predict friction reduction based on properties of the polymer, scaling the solution to different pipe diameters often was inaccurate (Sellin & Ollis, 1983)

Many early researchers agreed that a friction reducer must have three properties if it is to be effective: solubility, polymer linearity, and high molecular weight (Gordon, 1970; Hoyt & Fabula, 1964; Virk, 1975). The friction reducing agent must be soluble because otherwise its polymer relaxation frequency is not on the same time scale as the

formation of turbulent eddies. Linearity is necessary to properly absorb and dispel the energy from eddies, while higher molecular weight compounds provide better structural integrity of the molecules under turbulent flow. These necessary properties explain why PEOs and polyacrylamides are appropriate for reducing friction, but also why they perform differently. PEOs are very effective friction reducers due to their extreme linearity; that is, the only side groups on the polymer are simply hydrogen molecules (Pruitt, Rosen, & Crawford, 1966). This is notable since many shorter, functionalized molecules are not as soluble (Shetty & Solomon, 2009; Kjellander & Florin, 1981). Though PEOs have high linearity and can be dissolved as high-MW polymers, the MW per monomer is quite low, facilitating high degradation in turbulent flow (Hoyt & Fabula, 1964; Savins, 1964; Paterson & Abernathy, 1970). Polyacrylamide is a similar molecule to PEO in that is linear, soluble, and high-MW, but differs in having amide side groups (Pruitt, Rosen, & Crawford, 1966). This was thought to make the molecule more resistant to shear degradation, while still performing as effectively as PEOs, though the true reason for the difference in performance would not be discovered for decades. Incidentally, most long-chain polymer friction reducers experience even higher shear degradation at elevated temperatures in various solvents (Hamouda & Omotayo, 2007).

More recently, and with the advent of computer modeling and high-accuracy laser velocimeters, researchers have sought to more accurately characterize friction reduction. Use of laser velocimetry has enabled measurement of fluid velocities at a much finer resolution, and at much closer distances from pipe walls (Den Toonder, Hulsen, Kuiken, & Nieuwstadt, 1997). The development of computer models has also contributed to the understanding of the friction reduction phenomenon by allowing the use of much more complex equations and the ability to numerically solve them over very small grid sizes.

The more complete characterization of friction reduction provides a picture of the phenomenon as follows. Under normal conditions of turbulent flow, energy generated from fluid shear against the pipe wall promotes formation of turbulent eddies, which absorb more energy from the fluid and grow larger, finally dispersing and imposing forces on the pipe wall in an isotropic and spherical fashion – this is the source of increased pressure in the pipe due to higher friction and turbulent flow. Adding low concentrations of polymers yields dilute solutions in which the polymers can be treated as discrete molecules within the bulk fluid. These long molecules orient such that they are parallel to the direction of flow, and in the layer nearest the wall boundary they absorb the energy that would normally cause the newly-formed turbulent eddies to grow and eventually disperse. Earlier researchers hypothesized that the polymers absorbed the energy fully (Hoyt, 1972), but it was later discovered that the additives act not just viscously, but viscoelastically, like damped springs (Den Toonder, Hulsen, Kuiken, & Nieuwstadt, 1997). After absorbing the energy from the eddies, the polymers do allow it to be dispersed viscoelastically – much like a vehicle's shock absorber – but instead of being isotropically dispersed, the energy is anisotropically dispersed in a way that is much stronger in the direction of flow. This is why the addition of friction reducing polymers in a base fluid rapidly increases the flow rate and decreases the pressure of the system: the energy that would have been seen as friction pressure is now being used to essentially shunt a higher volume of fluid through the pipe due to the shift of the stress profile in the pipe.

2.4 FRICTION REDUCERS

2.4.1 Polyacrylamides

As for the application of the friction reduction phenomenon, the industry standard for reducing pipe friction pressure in hydraulic fracturing is to use either a polyacrylamide friction reducer emulsified in oil, or a variation of this, including acrylamide copolymers or granulated polyacrylamides (Ahrenst, et al., 2008). A new unique manifestation of this additive is stored in highly concentrated brine – instead of emulsified in oil – taking advantage of the polymer-coiling effect that brine has on polymer to keep viscosity low even in concentrated form (Ferguson, Anderson, Eichelberger, Hallock, Qiu, & Roell, 2013). Generally, polyacrylamide is added "on the fly" and in small concentrations – usually at or below one gallon or part per thousand (gpt or ppt) (Ercan & Ozbayoglu, 2009) – to create the ubiquitous "slickwater" in fracturing operations (Rimassa, Howard, & Blow, 2009). Polyacrylamides have been the standard for years, so it is obvious that researchers looking to recycle flowback water would start with this polymer type. The reason that friction reduction in brines is a problem, however, is that the salts prevent polymer molecules – and especially polyacrylamides – from unfurling and hydrating, thus reducing their effectiveness (Pruitt, Rosen, & Crawford, 1966; Ferguson, Anderson, Eichelberger, Hallock, Qiu, & Roell, 2013). This is manifested in increased polymer hydration time (Paktinat, O'Neil, Aften, & Hurd, 2011), reduced maximum friction reduction (Aften & Watson, 2009), and increased polymer degradation due to heat and brine content (Ke, Qu, Stevens, Bracksieck, Price, & Copeland, 2006) – which are generally only ameliorated by adding higher concentrations of polymer (Fox, Stouffer, & Utley, 2008). On the other hand, polyacrylamides are advantageous due to their customizability: depending on the percentage of amide groups, chain length, and ionic nature, the polymers can be tailored for specific base fluid

chemistries (Zelenev, Gilzow, & Kaufman, 2009). Additionally, due to the structure of the polymer – which is a carbon backbone with amide and carboxylic side groups, shown in Figure 5 – the molecules are fairly resistant to shear degradation and can perform well for extended periods. In fact, den Toonder and colleagues noted that it took nearly 20 hours of continuous flow in a lab to degrade a dilute polyacrylamide solution (1997).

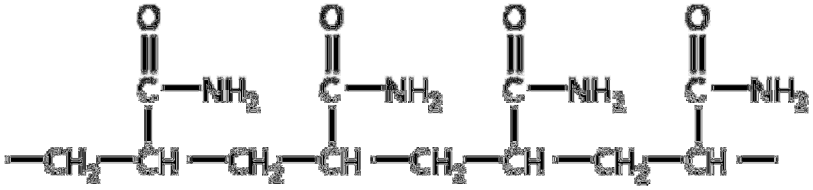

Figure 5 - Structure of Polyacrylamide (ZL Petrochemicals Co., 2012)

2.4.2 Surfactants

Aside from long-chain polymers like polyacrylamide and guar (which is mostly used as a proppant suspension agent nowadays), surfactants are also used as friction reducers in hydraulic fracturing. The ionic nature of surfactants, as well as their amphipathic structure (which includes a hydrophobic tail and a hydrophilic head), enables them to coalesce to form micelles of various shapes and sizes. These range from small spheres to long tubular structures, which have varying properties based on their shape (Shenoy, 1984) – since a good friction reducer must be a long molecule, then a long micelle can have a similar effect. Unlike long-chain polymers, the threshold at which surfactants begin to reduce friction by forming micelles can be lowered through the addition of electrolytes (i.e. higher salt concentrations), as opposed to the decrease in friction reduction efficiency seen with polyacrylamides in brines (Wang, Yu, Zakin, & Shi, 2011). Though the micelles can be broken up under increased turbulence, they can generally reform after the shear is lessened (Shenoy, 1984). Surfactants also have the

ability to suspend proppant, and are also much less likely to cause proppant pack or formation damage due to the reversibility of micelle formation. The main disadvantage of these additives is that they are fairly expensive, and also have the potential to change the wettability of the formation, leading to potential post-fracturing damage. This option was not considered within the scope of this research because surfactants are often tailored by chemical companies in rigorous and chemistry-focused development programs – the research instead focused on comparing a traditional friction reducer (polyacrylamides) to one that has not seen use in hydraulic fracturing and a novel and salt-tolerant polyacrylamide.

2.4.3 Polyethylene Oxide

The novel aspect of this research is the consideration of PEO as a friction reducer for hydraulic fracturing, an application which has been overlooked until recently (Dow Chemical Company, 2014). As stated previously, these polymers consist of a repeated ethylene oxide monomer, $(CH2CH2O)_n$, and have a wide range of molecular weights, which are related to the chain length and degree of polymerization. Commercially available PEOs span a wide range of molecular weights, from under 200 (usually called polyethylene glycol, or PEG) to 7,000,000 (Kjellander & Florin, 1981), all of which are soluble in water. Extensive research has not uncovered any utilization of PEOs as the primary friction reducer in hydraulic fracturing, though a recent product from Dow appears to use a high MW PEO for this purpose (2014) – no other studies with this product have been found as yet. PEOs have been used in both research and commercial applications since the discovery of their friction reduction potential in dilute polymer solutions. Many researchers considered PEOs to be the most effective friction reducer (Hoyt & Fabula, 1964; Hoyt, 1972) since they can achieve high friction reduction at very

low concentrations – only 2 ppm_w (parts per million by weight) (Pruitt, Rosen, & Crawford, 1966) – though the same extreme linearity that affords the molecule such effectiveness also renders it susceptible to shear degradation. For example, Pruitt and coworkers found that conventional fluid drivers like gear pumps degraded PEOs so quickly that they could not be used (1966). However, many uses have been proposed, tested, and sometimes implemented: increasing sewer capacity during storm events, reducing drag via application through boat hulls, facilitating transportation of hydrocarbons over long-distance pipelines (Sellin, Hoyt, Poliert, & Scrivener, 1982), and in higher concentrations for enhanced oil recovery (Nouri & Root, 1971). Importantly, PEOs are readily soluble in water and are not strongly affected by high salt concentrations – they still perform well in brines, unlike polyacrylamides (Sitaramaiah & Smith, 1969). This was observed over 40 years ago, yet seemingly forgotten with the rise and subsequent dominance of polyacrylamide usage in the fracturing industry. Sitaramaiah and Smith's brief results were the key in the decision to pursue the evaluation of PEOs for potential use in fracturing in this research.

On a molecular level, PEOs function more effectively than nearly any other water-soluble polymer on a per-weight basis due to their unique structure. Kjellander and Florin noted that the structure of liquid water actually forms a near-perfect "cage" around individual molecules, in the case of dilute polymer solutions (1981). Considering that other closely related polymers such as polymethylene oxide and polypropylene oxide are completely insoluble, this is an unexpected phenomenon. Additionally, since solubility in brine under standard conditions is more entropically favorable than the polymer being coiled by the reduced solvency, coiling would be minimal in salt solutions – an important property when comparing PEO with other polymers, since it is this coiling that inhibits friction reduction (Pruitt, Rosen, & Crawford, 1966). The performance of PEO is actually

even greater than its molecular weight and linearity would suggest: according to Shetty and coworkers, when predicting friction reduction based on these properties, its effectiveness is significantly under-predicted (2009). Through various experimental and modeling techniques, researchers in the 2000s deduced that this is due to the tendency of PEO to agglomerate – much like surfactants – into larger micelles whose effective molecular weights are far higher than for the individual molecules. Therefore, when the performance wanes after exposure to shear forces, it is likely the results of the degradation of these micelles rather than actual scission of the carbon backbones of the molecules (Shetty & Solomon, 2009). The researchers' experimentation with salts that disable the agglomeration of PEOs adds to the important conclusion that PEOs not only act as long-chain polymers in solution (like polyacrylamides), but they essentially work better than they should in proper solutions because they behave similarly to surfactants in forming aggregate micelles.

PEOs have one more important property that makes them potentially attractive as oilfield additives: inverse solubility. That is, while most solutes become more soluble with increasing temperature, PEOs actually appear less soluble at elevated temperatures (Kjellander & Florin, 1981). At very high temperatures, they once again dissolve, making this property technically a "solubility gap." For practical purposes, however, it is said that PEO solutions have a "cloud point temperature," or CPT, where a heated solution begins to look cloudy as the polymer comes out of solution (Bland, Smith, Eagark, van Oort, & Dharma, 1996). This property is theorized to stem from the entropy balance in a PEO solution: at low temperatures, the solution of the polymers with the water "cage" is entropically favorable, but as temperature increases the solution destabilizes and can no longer hold PEO molecules within the water lattice (Kjellander & Florin, 1981). The phase change is not immediately completed though, and as temperature is increased

above the CPT, more polymer precipitates until it is a completely separate phase (Bland, Smith, Eagark, van Oort, & Dharma, 1996). Decreasing temperature will completely reverse the effect and allow the PEO to go back into solution. Ion type and concentration, polymer weight and concentration, and addition of a co-dissolved polymer can all affect the CPT, generally by lowering it (Florin, Kjellander, & Eriksson, 1984).

As an important consideration for developing a novel potential friction reducer for hydraulic fracturing, compatibility with shale formations must be assessed. The benefit of using a salt-tolerant and effective friction reduction agent is lost if the formation or proppant pack is damaged after a fracturing operation. This is the case with much of the current additives used in industry: when polyacrylamide, guar, or even surfactants are added to reduce friction, a breaker is usually included in the fluid formulation to ensure the polymers do not degrade fracture conductivity, though traditionally it was thought that the small concentrations of these additives could not appreciably damage the formation (Carman & Cawiezel, 2007). Another approach to preventing formation damage from friction reducers is to design the polymer (in this case, a polyacrylamide) to be more susceptible to breakage (Sun, Wood, Stevens, Cutler, Qu, & Lu, 2011). Apart from damaging the proppant pack, operators also design fracturing jobs to ensure that the injected fluid does not damage the formation due to water invasion and subsequent ion exchange within the shale's clay laminae (Blauch, 2010). This can lead to the problems of shale swelling, proppant embedment, or mobilization of fines from the shale that can then damage the proppant pack (Alramahi & Sundberg, 2012; Pedlow, 2013). Since PEOs are known to form large micelles above their CPT and since high temperatures are common in shale formations, it is important to understand how these micelles could affect shale interaction. It is already known that the salts present in flowback water can stabilize shale (Rimassa, Howard, & Blow, 2009; Mimouni, 2014). At least for lower-

molecular weight PEOs (called polyglycols), it may be possible to engineer the solutions using salts to that the PEOs cloud out just as the fluid invades the formation. This leads to a phenomenon dubbed the "thermally activated mud emulsion (TAME) mechanism" in the drilling fluids field, wherein polymeric micelles form in a small layer just beyond the shale-water interface at temperatures high enough to facilitate their formation (Downs, van Oort, Redman, & Ripley, 1993). This TAME system was further developed to work most effectively with polyglycols (with MWs of 500-2000) in already-inhibitive KCl brine (Bland, Smith, Eagark, van Oort, & Dharma, 1996). Our hypothesis is that if the PEOs selected for friction reduction have a similar structures and clouding behavior, what was originally a potential friction reducer could actually be a multifunctional fracturing additive.

This method of shale stabilization that blocks fluid invasion is distinctly different from the shale stabilization offered by polyacrylamides, which keep shale together after water invasion via cationic polymeric bridging (Aften, Paktinat, & O'Neil, 2011; Wingrave, Kubena Jr., Douty, & Cords, 1987). For the smaller grades tested by Bland and colleagues, the size of the PEO (related to the MW) not only allowed the molecules to invade the shale and form a micellular blockage, but also to flow back and/or degrade following operations (Bland, Smith, Eagark, van Oort, & Dharma, 1996). This may not necessarily be true for the PEOs that reduce friction so effectively, as they are many orders of magnitude larger – no research has been found regarding experimental determination of larger PEOs' ability to block water invasion of shale. Additionally, the only viable method for potential downhole cleanup of these molecules seems to be reducing the temperature, which is not possible. However, smaller PEOs indeed are biodegradable, and larger ones can be reduced to benign and biodegradable products under high temperatures (Madorsky & Straus, 1959; Calahorra, Cortazar, & Guzman,

1985), generally by random carbon-carbon bond scission rather than stepwise depolymerization (Mantzavinos, Livingston, Hellenbrand, & Metcalfe, 1996). Optimum temperatures for degradation are in the range of pyrolysis though, and may not be encountered downhole. Fortunately, if PEOs flow back to the surface, the molecules are nontoxic – in fact, they are currently used as soluble pharmaceutical tablet coatings (Dow Chemical Company, 2002).

Overall, the ability of PEOs to reduce pipe friction more effectively than any other known water-soluble polymer along with their tolerance to high salt concentrations makes a compelling case for experimental investigations, especially when considering the possibility that they may also be effective as shale stabilizers. If PEOs are indeed more effective in a fracturing industry-style flow loop and in stabilizing shales, then perhaps appropriate attention should be given by the industry. If, however, polyacrylamides are found to be superior shale stabilizing agents compared to PEOs, then either further optimization of a PEO blend should be considered, or the focus in friction reduction research should indeed continue to be optimization of polyacrylamide formulations and applications.

Chapter 3: Experimental Methods

To assess the suitability of friction reducers for potential use in flowback and produced water, various experiments were conducted in order to observe performance in various brine solutions: deionized (DI) water, sodium chloride (10 and 20% by weight), calcium chloride (5 and 10% by weight), and a multisolute brine of 7.4% NaCl and 1.76 CaCl2 to simulate a multivalent flowback water. These experiments primarily focused on friction reduction in a flow loop, but also covered shale stabilization abilities and other chemical properties of the additives.

3.1 Principles of Friction Reduction

Since the primary use of friction reducers in fracturing operations is to reduce pipe friction pressure, a flow loop was designed to simulate field conditions at a lab scale. A flow loop is essentially a pump-powered recirculating system that allows for measurement of the friction-induced pressure differential across a length of pipe, ΔP. This metric is measured over the course of an experiment for a friction reducer in a test solution, then compared to the ΔP measured for the base fluid with no friction reducer added. The proportional reduction in this value – which must be measured at a constant flow rate – is given as the friction reduction percentage (FR%), first given by Hoyt (1972). Mathematically, this is represented as:

$$FR\% = \frac{\Delta P_{base} - \Delta P_{test}}{\Delta P_{base}} \qquad \text{Eq 4}$$

where ΔP_{base} is the average pressure drop for the base fluid measured over one minute, and ΔP_{test} is the time-dependent pressure drop for the fluid with friction reducer. The friction reduction percentage is calculated and plotted versus time. This is the most basic

method for calculating friction reduction, and is the current industry standard for testing friction reducers. As indicated previously, other methods for quantifying friction reduction have focused on the change in Reynolds number or Fanning friction factor. However, this is not an ideal approach to use for comparing fluids that may have different properties (i.e. Newtonian or non-Newtonian).

3.2 SYSTEM COMPONENTS

Flow loops contain a variety of components including a pump, tubing, flow meter, pressure transducers, storage reservoir, a data acquisition system, and other appurtenances. A schematic of the flow loop system is shown in Figure 6. A key to the design of the system was to ensure that the Reynolds number was sufficiently high to create friction reduction in a dilute polymer solution (i.e. decrease in Fanning friction factor *f*). The data presented in Figure 7 shows that this phenomenon is only observed at

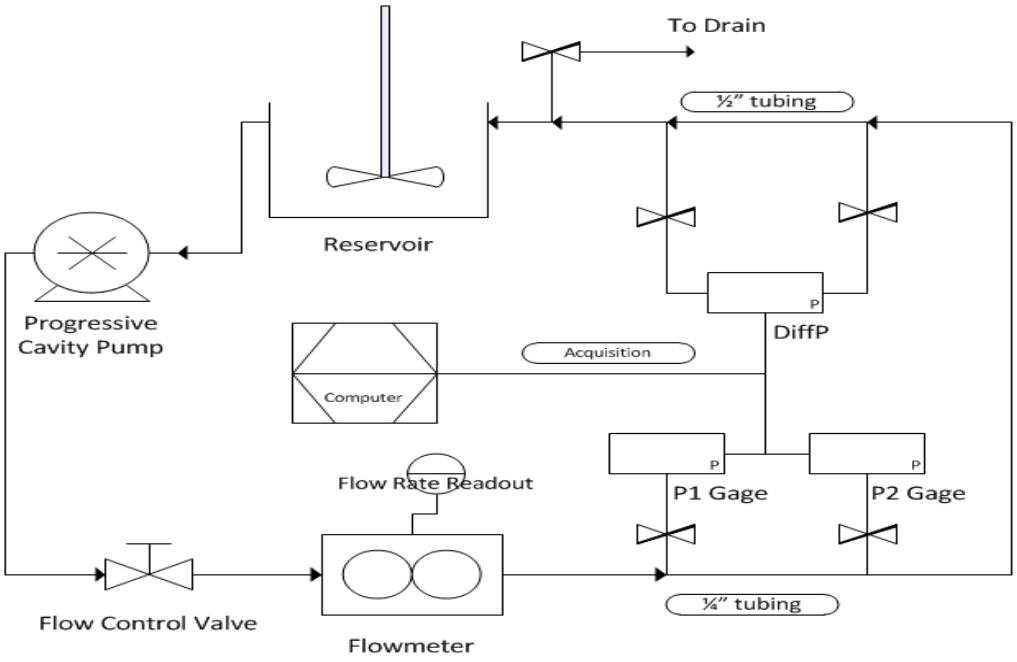

Figure 6 - Schematic of Flow Loop

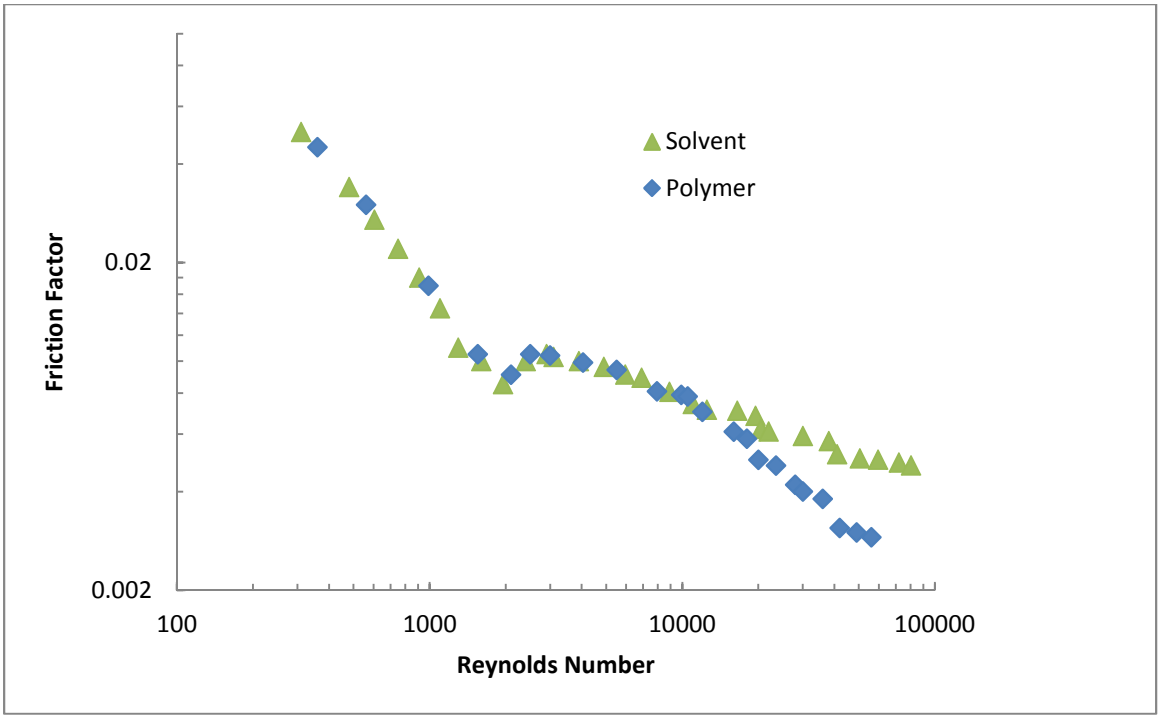

Figure 7 – Variation of Friction Factor in Friction Reduction Solutions Depending on Reynolds Numbers, Adapted from Virk (1975)

Re values above 4000, and becomes more pronounced with more turbulent flow.

The individual elements of the system were designed as follows:

- **Pump:** A progressive cavity, or "Moyno," pump was selected for its abilities to pump a wide range of fluid viscosities, to handle potential particles, and to provide pulsation-free flow, as is well proven in routine oilfield service (mostly for supplying drilling muds). The most important reason for choosing this type of positive displacement pump was the negligible shear imparted to the fluid by the rotor and stator, since shear forces can lead to polymer degradation. It is important to minimize any polymer degradation due to shear and to ensure that any degradation occurs in the straight pipes. The pump used in the main flow loop was designed to handle a differential pressure of up to 140 psi and to be able to

pump anywhere from 2.5 to 10 gallons per minute (gpm). Other specifications were that it should be able to handle slightly viscous fluids (up to 5 cp) and elevated temperatures (up to 190°F). The pump used was a 2LL4 (2-stage pump) from Liberty Process Equipment.

- **Flow Meter:** The flow loop utilized a RCDL M25 nutating-disc type flow meter from BadgerMeter Inc. Though a coriolis flow meter is ideal for measuring nearly any type of fluid, this flow meter was prohibitively expensive. In the main flow loop, the flow rate is shown on an ER-420 model digital display to three decimal point precision.
- **Pressure Transducers:** The loop contained Rosemount 2051 conventional and differential model pressure transducers, calibrated to a range of 0 to 200 psi. These transducers had an accuracy of ±0.065% of the range.
- **Piping:** All pipes and fittings were 316 stainless steel (Swagelok). Two pipe sizes were tested since both had been used in previous work: ¼" and ½" outer diameter (OD). The inner diameters of the pipes were 0.18 and 0.43 inches, respectively. Lengths of 1.5 ft for both pipe sizes were used based on the minimum length to register a pressure drop for the specified parameters, and to minimize the space occupied by the system. Unfortunately, due to an early error in calculation of the friction factor, these sizes are mutually incompatible: high flow rates push the pressure too high due to the smaller diameter pipe, and low flow rates do not register a measurable or consistent pressure drop in the larger diameter pipe. Therefore, differential pressure data is only for the ¼" pipe at a lower flow rate than originally envisioned, though still produced fully turbulent flow. As for sharper bends between the pipe sizes and other system elements, 1" hose from Parker was utilized to ensure minimal extra friction pressure and shear.

- **Reservoir:** Though most previous research has utilized a fairly large mixing reservoir (see Appendix A: Criteria for Flow Loop Design from Literature), it was determined that five gallons was sufficient, and the smaller size was preferable to reduce waste from experiments. A plastic bucket was used for ease of polymer addition, but a 316 stainless steel pail was used in a later modification for high temperature tests. To ensure a fully mixed reservoir, an overhead mixer was used – a Talboys Model 101 with 1/75th hp, a double impeller, and adjustable motor.
- **Data Acquisition and Recording:** The pressure transducers were wired to a National Instruments USB-6008 data acquisition unit and recorded on the company's LabVIEW software (2009).
- **Other Considerations:** The lines to all pressure transducers were isolated with butterfly valves and filled with mineral oil to minimize dead space in the lines; to prevent residual polymer solution from leaking back into the system from these lines (Hoyt, 1972). These valves are only opened while running a test. Additionally, a waste line is included to more effectively clean and drain the system.

The total volume of the system was estimated to be 5 L, ±200 mL. To obtain this value, the system volume (minus the reservoir) was measured in three ways: by measuring the drained volume using compressed air, calculating the volume using known inner dimensions of piping and elements, and using a tracer to measure the residence time in the system.

3.3 FRICTION REDUCERS

The friction reduction additives used in the experiments are shown in Table 2. All were provided as samples from their respective companies, and were added in

Table 2 - Friction Reducers Used in Flow Loop Experiments

Friction Reducer	**Manufacturer**	**Polymer Type**	**Charge**	**Form**	**Mol. Weight**
DR3046	SNF, Inc.	Polyacrylamide	Anionic	Oil inverse emulsion	"high"
DPFR	Nalco	Polyacrylamide	Not known	Concentrated brine dispersion	"high"
WSR301	Dow	Polyethylene Oxide	Nonionic	Fine powder	$4x10^6$ g/mol

concentrations of 0.1% (weight basis for PEO, volume per weight basis for polyacrylamides). As previously mentioned, these additives were chosen to represent a typical and reasonably salt tolerant polyacrylamide (DR3046), a novel and very salt-tolerant polyacrylamide (DPFR), and a novel polymer that has seen very limited use in fracturing (WSR301). Note that all the polymers used are considered nontoxic and fully soluble in water.

3.4 EXPERIMENTAL DESIGN

Using experimental parameters that other researchers have used in their friction reduction experiments, typical values for flow rate, Reynolds number, and measureable pressure drop were determined for sizing the various elements of the system. A summary table of the literature values used is presented in Appendix A: Criteria for Flow Loop Design from Literature. Though many parameters were important in designing the loop, only a few had to be predetermined. Based on literature values, a Reynolds number range of 70,000 to 100,000 was selected as the basis for design, as well as a pipe outer diameter of ¼" to ½". This Reynolds number range is indicative of the turbulence encountered in

industry flow loops, and the pipe sizes selected are commonly used in flow loop testing. From here, using the modified Bernoulli equation (for real fluids) and Colebrook's experimental fit for the friction factor, the flow rate necessary to achieve the desired Reynolds number range in the pipe size desired was determined, as well as the pressure drop that would be expected from these parameters. The modified form of Bernoulli's equation that includes friction factor is as follows:

$$\Delta P = \rho g \left(\Delta z + f \frac{L V^2}{D 2 g} \right) \quad \text{Eq 5}$$

where ΔP is the pressure drop, ρ is the density of the fluid, g is the gravitational constant (9.8 m/s2), Δz is the change in height, f is the friction factor, L is the length of pipe over which the pressure drop is measured, V is the fluid velocity, and D is the pipe's diameter. Colebrook defined the friction factor over all Reynolds numbers as follows (1939):

$$\frac{1}{\sqrt{f}} = -2 * \log \left(\frac{\epsilon / D}{3.7} + \frac{2.51}{Re\sqrt{f}} \right) \quad \text{Eq 6}$$

where ε is the pipe roughness and Re is the Reynolds number. This equation must be solved iteratively for all transition and turbulent flows, but is greatly simplified for laminar flows. It must be noted that these two equations apply to Newtonian fluids, whereas dilute solutions of friction reducers generally do not behave as such. The rationale for using these equations, then, is as follows: if the highest pressure drop (and therefore, one of the major limiting design factors) is observed when using the base Newtonian fluid, then the flow loop should be designed around the "worst case scenario," which would result from the densest base fluid to be studied.

Like the hydraulic characteristics used in the experimental design, the concentration of friction reducer to be added was also taken from common values used in the literature – both from lab and field work. For polyacrylamides, it was decided that 0.1% by volume should be used. The majority of slickwater operations and lab tests use

lower concentrations, but typically increase the amount when brine solutions are used – therefore, we rounded up to 0.1% (expressed in the industry as gallon per thousand gallons, or gpt). As for PEOs, though grades of much smaller MW – called polyethylene glycol or polyglycols – are used in concentrations of up to 5% by weight for wellbore stability in drilling operations (Bland, Smith, Eagark, van Oort, & Dharma, 1996), high-MW PEOs achieve high friction reduction using significantly lower concentrations. The highest concentration found in the literature for use of PEO for friction reduction is 940 ppm_w (Virk, 1975) and the minimum concentration needed to achieve aggregation (and therefore better friction reduction) is 620 ppm (Shetty & Solomon, 2009). To take advantage of the fact that PEOs are very effective at low concentrations, a 0.01%, or 100 wppm (all percentages for PEOs are on a mass basis) was selected for the low concentration; the high concentration of 0.1% was chosen based on the minimum concentration required for aggregation by Virk (1975).

After running initial tests with PEOs at 0.01%, it was soon apparent that the turbulence in the flow loop caused these solutions to show rapid degradation, so a higher concentration of 0.1% was used. This concentration is still low enough to be considered a "dilute solution" and ensure the friction reduction mechanism is not overshadowed by the viscosity that arises in more concentrated polymeric solutions. A few PEOs of varying molecular weight were evaluated over the course of testing, but the primary one used (Polyox WSR301) has a molecular weight of 4,000,000 g/mol.

3.5 EXPERIMENTAL PROTOCOL

The test procedure used for testing the friction reduction percentage is as follows. First, the system must be cleaned from any previous tests by flushing with tap water and ensuring the reservoir is cleaned. After the loop is flushed and filled with clean water, it

is then flushed and filled with about 3 gal of DI water. From here, the reservoir is filled to the desired amount (6 L for plastic bucket, 7 L for steel pail), and the pH of the water is adjusted by addition of dilute hydrochloric acid if necessary. For brines containing $CaCl_2$, the pH must be under 6 to ensure the salt is completely dissolved. While both the mixer and pump are running, any salt needed to make up the base brine is added and allowed to mix and dissolve. After preparing the base fluid, the baseline test is run for one minute at three gpm – the flow rate is monitored and adjusted as need to ensure it is constant, establishing ΔP_{base}. Once the friction pressure drop is recorded for the base fluid, the friction reducer is added instantaneously and the response is recorded for 10 minutes, again while keeping the flow rate constant at three gpm. There is often a dramatic rise in flow rate as the friction reducer hydrates and dissolves. Finally, the FR% over time is calculated from the ΔP at each time step as a proportion of the baseline ΔP_{base} average.

Upon completion of an experiment (or set of experiments), the entire system should be cleaned. Cleaning the system involves flushing with at least 10 gallons of tap water, then either draining the system or moving on to subsequent tests by then flushing with DI water. The reservoir itself, as well as the removable inlet and outlet pipes, is scrubbed with a mild lab cleaner. Occasionally the system is cleaned with a dilute bleach solution to prevent any buildups of polymer in the tubing.

3.6 PRELIMINARY TESTING

Concerns regarding baseline test repeatability arose, especially since other researchers had noticed gradual fouling of their systems (Hoyt, 1972). This was also of interest since industry lab flow loops are periodically cleaned by flushing with a dilute bleach solution, which was also performed for this flow loop. A collection of five random DI water baseline tests where the flow rate was not controlled and varied from 2.985 gpm

to 3.015 gpm, as well as four random tests where the flow rate was more consistent between 2.995 and 3.005 gpm, was subject to statistical analysis to assess reproducibility. Using the Kruskal-Wallis test, the calculation of FR% from a specific DI water run with friction reducer was found to be unaffected when using any of the time-varying pressure data from controlled baselines, as well as when using any of the data from an uncontrolled baseline test. These results highlight the reproducibility of the results. Moreover, the implications of this analysis are that it is not necessary to conduct a DI baseline pressure measurement for each experimental test. Therefore, the test protocol was continued for all subsequent experiments.

It must be noted that not all of the polymers investigated could be added instantaneously. For the polyethylene oxides (PEOs) in their powdered form, it was necessary to first dissolve them in the base fluid for one hour (or two, if the concentration was higher than 0.1 wt%). This was determined by altering the mixing time and observing which mixing time yielded the best performance for the shortest time. Figure 8 shows the results of this test, where it is evident that one hour is the ideal mixing time, since it yields a higher FR% than 0.5 hrs, but takes less time than 1.5 hrs. After numerous tests were conducted using the pre-mixing approach for the PEO, it was decided to evaluate the use of an appropriate dispersant for more convenient and instantaneous addition of PEO to the flow loop. According to the Dow Chemical Company, which manufactures the product, it is known that the polymer clumps when added directly to water (2013), an observation noted in this research as well. Though early researchers working with Polyox (the trade name of the PEOs) solved this problem by preparing concentrated solutions of PEOs for storage, then diluting them, it was soon discovered that these solutions spontaneously degrade in their containers (Pruitt, Rosen, & Crawford, 1966). Instead, it was recommended to use either an alcohol such as 2-butoxyethanol or

isopropanol, saturated brine, or a lower-MW glycol that is liquid at standard temperature, such as polypropylene glycol (Dow Chemical Company, 2013). Dispersions were prepared using both 2-butoxyethanol and polypropylene glycol 425 (PPG), but the former was not compatible with many elastomers, including the one in the pump used in our experimental setup. Therefore, a 5:1 mass ratio of PPG to PEO was employed. This was found to dissolve quite rapidly when added to the flow loop. A discussion of this additive's effect on the friction reduction and other properties can be found in Chapter 4: Results and Discussion.

3.7 DESIGN MODIFICATIONS

During the course of friction reducer testing, equipment failure necessitated the construction of a new flow loop as a backup plan in case the original one could not be restored to working order. The second system was designed for tests at higher Reynolds numbers and turbulence, to ensure redundant pressure readings from two pipe diameters, and to improve control and monitoring of the flow rate. The following components were upgraded:

- **Pump**: The new pump is more powerful (3hp vs 2hp), which affords higher flow rates – up to 20 gpm, not accounting for pressure limitation. In addition, the new control unit allows for both monitoring and control via LabVIEW software.
- **Piping**: Since the two pipe diameters were originally too different to be used at the same flow rates, the new flow loop has 1/2" and 3/8" OD piping. Additionally, to ensure minimal interference from flow pulsations and turbulence that result from diameter changes, the entrance and exit lengths to the pressure measurement sections are one hundred times the inner diameter. Rounded up, this

means that each pipe has a 5 ft entrance and exit section surrounding a 10 ft pressure drop measurement section.

- **Safety**: Using a positive displacement pump with a fluid that has the potential for particle formation (i.e. above the cloud point) that could clog the pipes, it is imperative to use a pressure relief valve to prevent any damage to the pump or injury to the operator. The Swagelok sourced valve is set to 140 psi, which is also the maximum sustained differential pressure rating of the pump.
- **Data Acquisition:** A new LabVIEW program includes the ability to store baseline values and calculate FR% in real time, and uses a feedback loop to maintain constant flow rate.

Chapter 4: Results and Discussion

4.1 RESULTS

4.1.1 Baseline Friction Reducer Performance in Deionized Water

The results of running the polyacrylamide DR3046 in DI water at normal concentration (0.1% by volume) and a lower concentration are shown in Figure 8 to compare to PEOs' ability to reduce drag at very small concentrations (0.01% by volume). As can be seen, the apparatus produced the typical data associated with the instantaneous injection, hydration (to maximum FR%) and subsequent degradation of the polymer, seen in many studies on industry lab flow loops. The inconsistencies in the 0.1% plot are due to occasional adjustments of the flow rate using the manual needle valve, which were not always smooth.

In addition to confirming that the flow loop could handle addition of polyacrylamides instantaneously, it was also necessary to determine the proper method of PEO addition, since methods in the literature were quite varied. From lab experience – and as mentioned in Chapter 3: Experimental Methods – one hour of pre-mixing was the ideal preparation time for 0.1% (by weight) concentration of PEOs, but we wanted to optimize a standard concentration of PEOs as well. Though 0.1% and 0.01% had already been decided upon, we realized that the maxium potential friction reduction could perhaps be reached with more or less polymer, since a concentration too high could create a solution with too much viscosity while too dilute a solution might not have enough polymer to reach the minimum concentration necessray for aggregation behavior. As can be seen in Figure 9, the concentrations chosen were considered appropriate when compared data from tests conducted with 50% less and 50% more polymer. Note that there are two PEOs shown: WSR301 (MW=4,000,000) in red shades and WSR303 in

blue shades (MW=7,000,000). The WSR303 was mixed for 3 hrs (due to its decreased ability to dissolve in pure water) and the WSR301 was mixed for 1 hr. From the graph, it is evident that the optimum concentration for both PEOs is approximately 0.1%, since lower concentrations resulted in significant degradation over the course of a 10-minute test, and higher concentrations contribute too heavily to the viscosity of the solution. Thus, all remaining tests were conducted at 0.1%, since it was clearly the most effective concentration both for highest average friction reduction and resistance to shear.

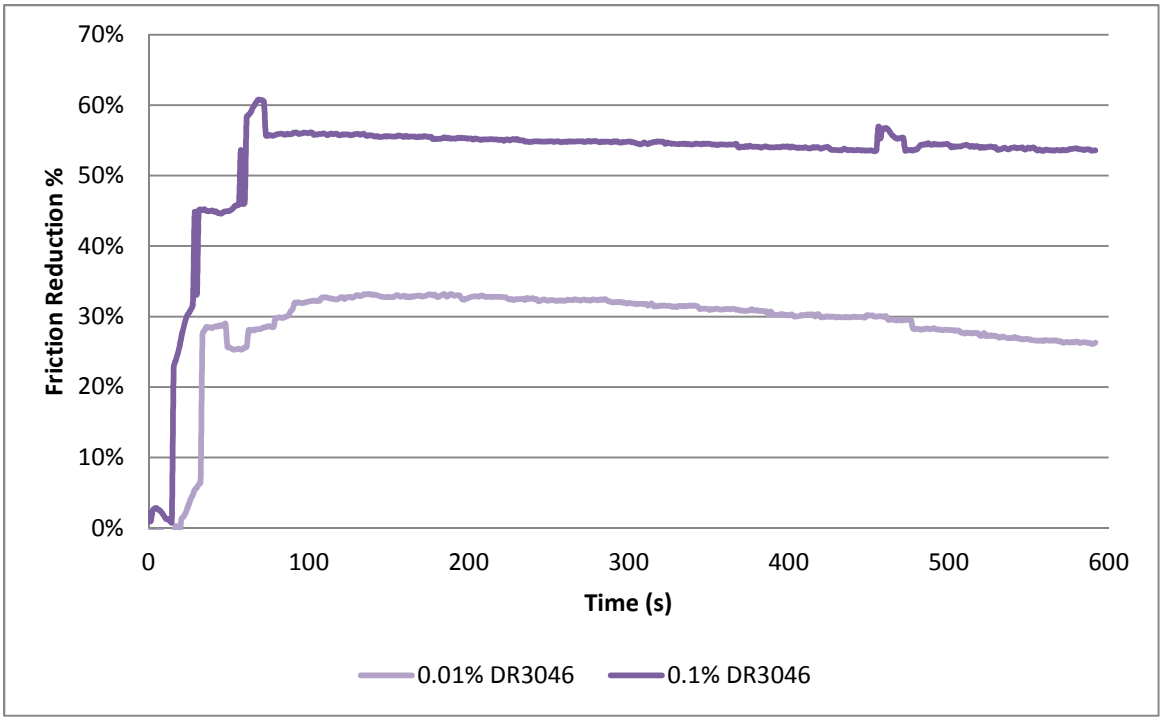

Figure 8 - FR% over Time for Typical Anionic Polyacrylamide at Normal and Low Concentrations in DI Water

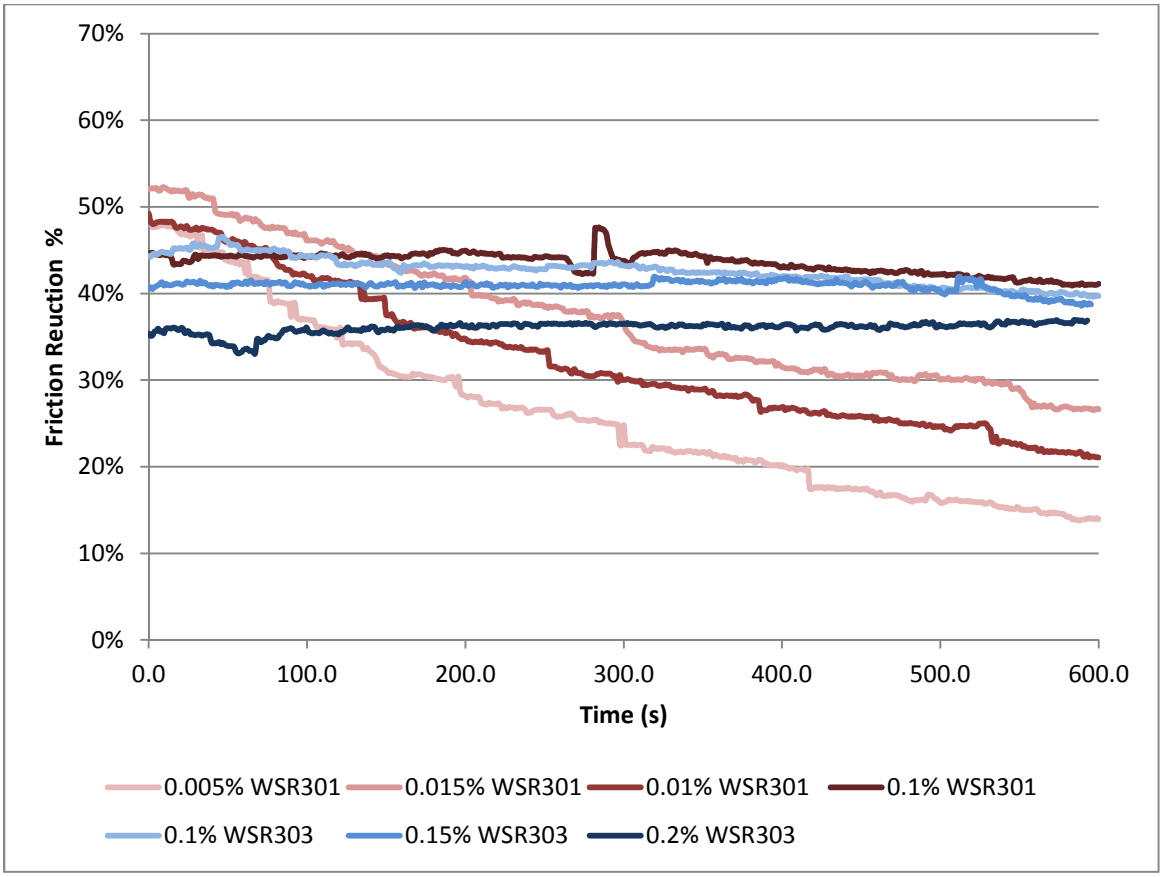

Figure 9 – Variation Testing for PEO Concentrations

Before testing the range of friction reducers selected for comparison, a few different grades of PEO were tested. The goal was to test the hypothesis that higher molecular weight PEOs would be reduce friction more effectively. However, the results showed that in the range from 1,000,000 to 7,000,000 g/mol, friction reduction was relatively similar when mixed at 0.1% with DI water. the 4,000,000 g/mol PEO (WSR301) performed just as well as the highest MW polymer, as shown in Figure 10; it was easier to dissolve, however. Therefore, in the interest of optimizing usability and efficiency, WSR301 was used in the majority of PEO tests.

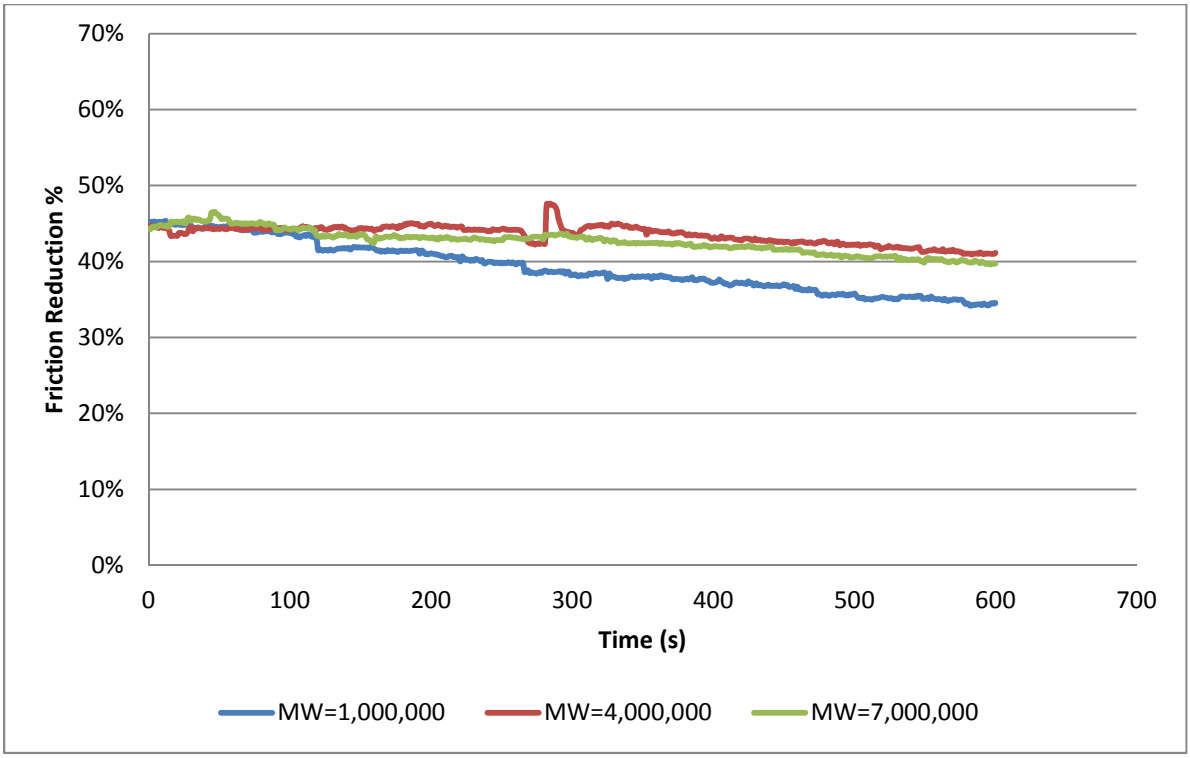

Figure 10 - 0.1% PEOs in DI Water

The next series of experiments compared peformance of the three different friction reducers. As shown in Section 3.3 Friction Reducers, a reasonably salt-tolerant anionic typical polyacrylamide (DR3046), a novel and very salt-tolerant polyacrylamide stored in concentrated brine (DPFR), and a high-MW PEO (WSR301) were evaluated. The subsequent section showcases the differences in performance between these polymers in various base brines. Note that any mention of WSR301 (the PEO) will refer to pre-mixing the polymer in the base solution for 1 hr.

The graph shown in Figure 11 displays the variation of friction reduction percentage over time for all three additives at 0.1% and 0.01% (by volume for DR3046 and DPFR, by mass for WSR301) in DI water. Though not particularly relevant for field application, these plots highlight the effectiveness of the PEO (by weight). Looking at the

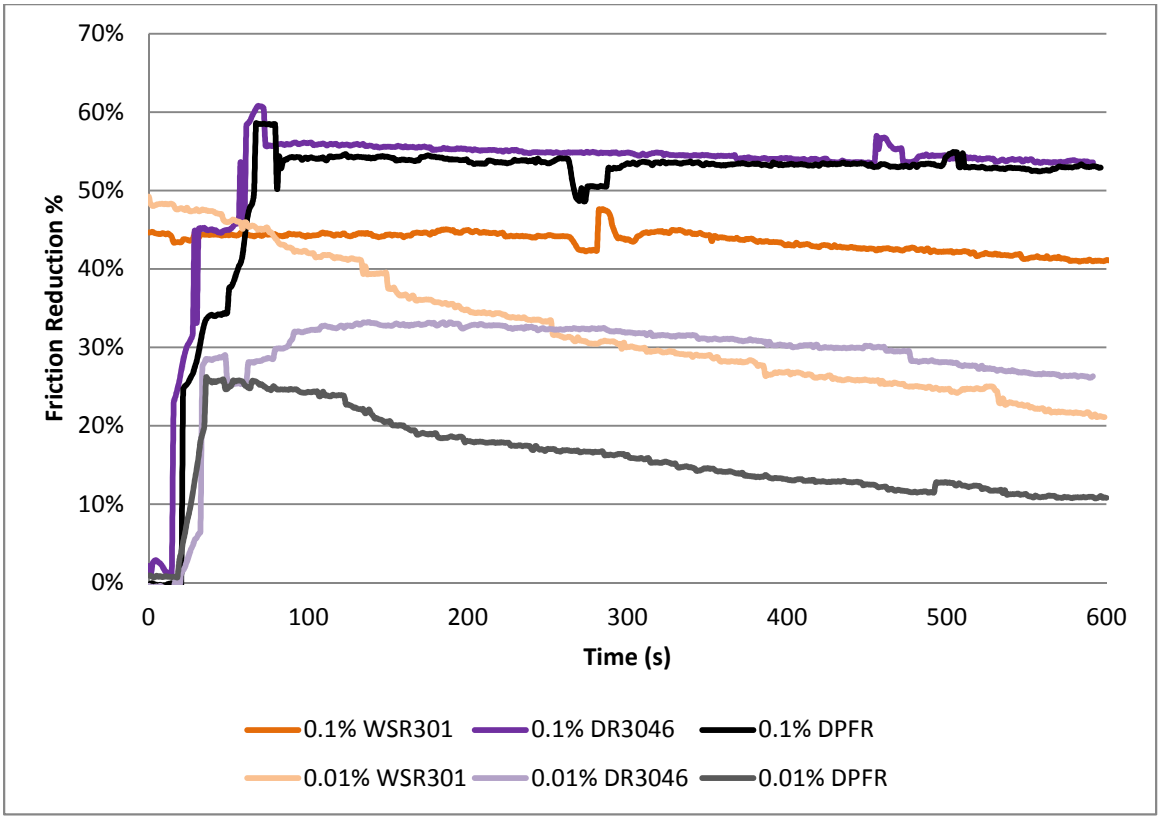

Figure 11 – Comparison of Friction Reducers (DR3046, DPFR, WSR301) in DI Water at 0.1% and 0.01% Polymer Concentrations

time period before 250 seconds, it is clear that when comparing just the low concentrations of the friction reducers, PEO outperforms the polyacrylamides, though it is eventually degraded by shear. This corroborates early research into friction reduction that showed PEOs as being very effective friction reducers even in dilute solutions (down to 2 ppm). The poor performance of the polyacrylamides could be attributed to the fact that many salt-tolerant polyacrylamides are actually only effective at high ionic strength – otherwise, they may not be well suited to pure water. Indeed, DR3046 in particular, is recommended only for use in brines.

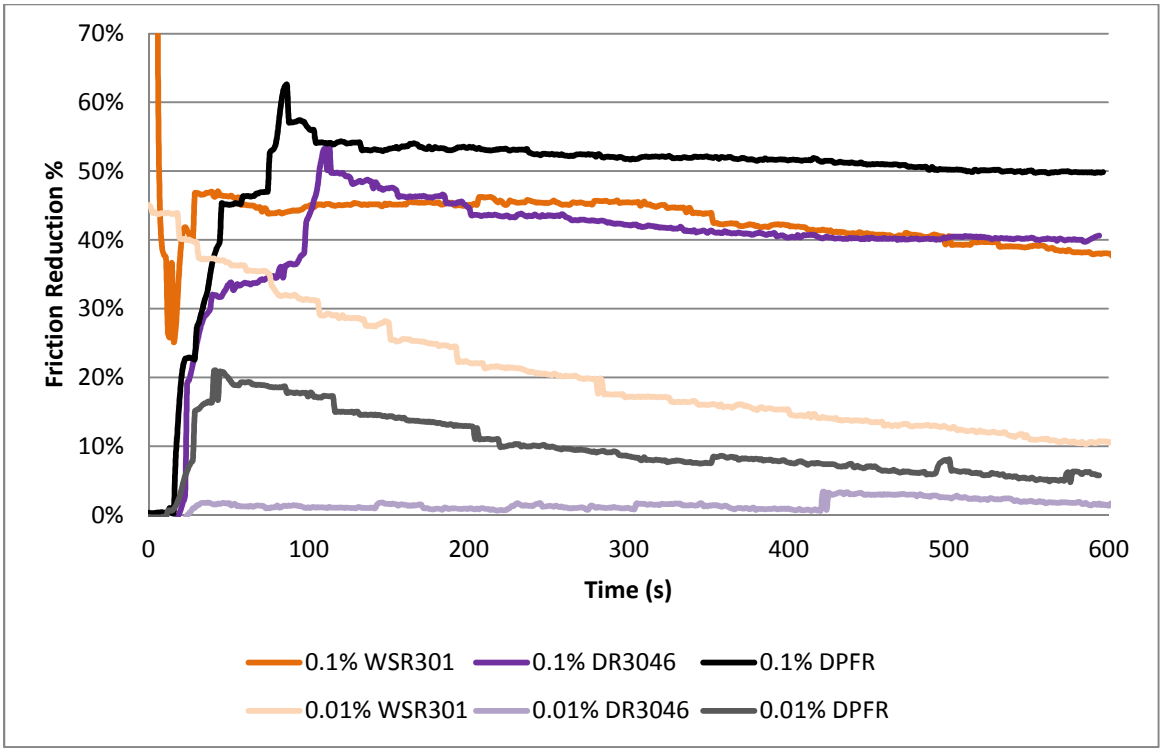

Figure 12 – Comparison of Friction Reducers (DR3046, DPFR, WSR301) in 10% NaCl at 0.1% and 0.01% Polymer Concentrations

4.1.2 Impact of Brines on Friction Reducer Performance

Figure 12 shows the same additives and concentrations as in Figure 11, but the base fluid here is 10% sodium chloride (by weight). It can be seen that this high concentration of NaCl (higher than often encountered in the field when reusing brines) causes a loss in friction reduction efficiency in the typical polyacrylamide (DR3046), especially in the low concentration. The novel DPFR still performs quite well, while the PEO – though inferior in this solution – is also fairly high-performing. At the low concentrations, only the PEO is able to achieve any reasonable level of friction reduction for the first few minutes. Figure 13 shows results from the same additives but in 20% NaCl instead, and only at 0.1% concentrations, since the 10% NaCl tests showed that the lower concentration is not effective. At this very high salt concentration, no friction

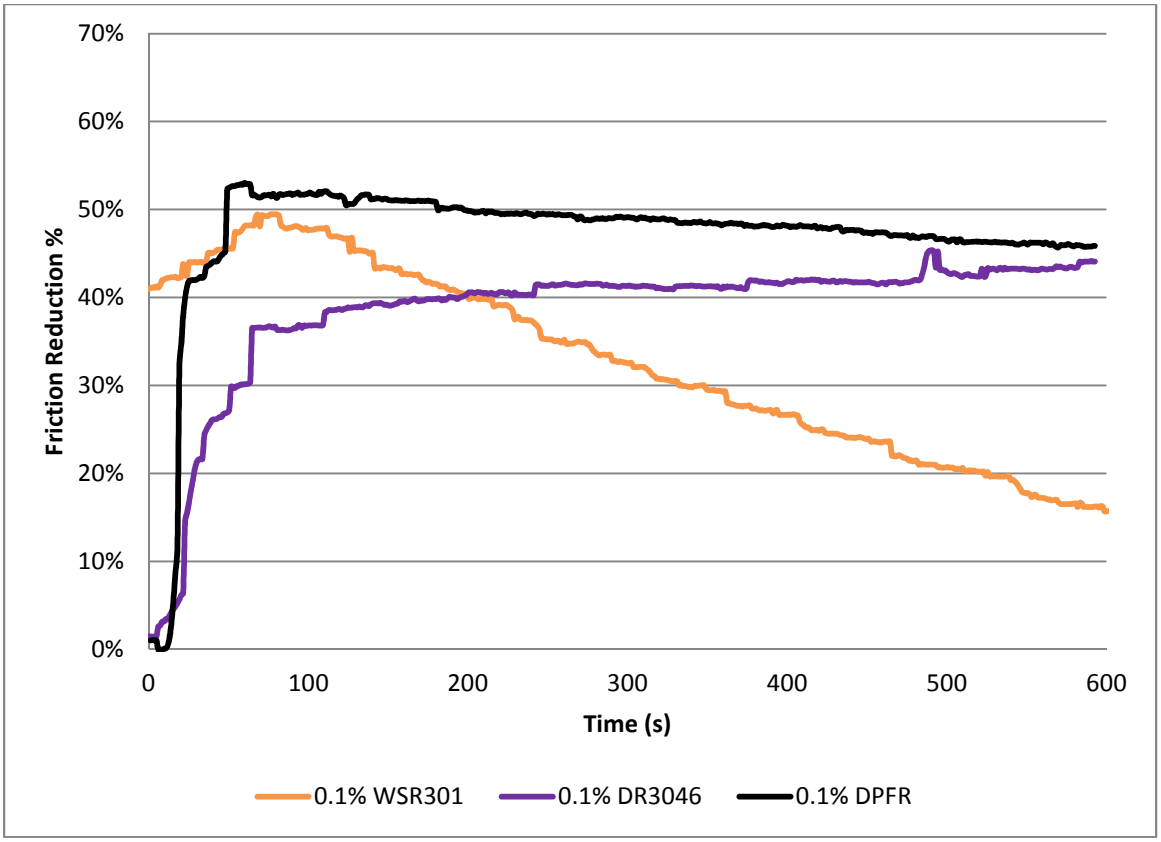

Figure 13 – Comparison of Friction Reducers (DR3046, DPFR, WSR301) in 20% NaCl at 0.1% and 0.01% Polymer Concentrations

reducers perform better than 55%, but all are comparable for the first few minutes. PEO is clearly degraded over the course of the run, possibly due to the effect of ions on the entropically favorable solution and aggregation of PEO molecules. One possible explanation is that, if it becomes more difficult to dissolve PEO due to the presence of a cosolute, then the aggregates cannot withstand the shear, or perhaps even form properly.

Continuing the comparison of friction reducers in various salts, Figure 14 and Figure 15 show the same friction reducers in 5% and 10% $CaCl_2$ respectively. Though the typical (and salt-tolerant, as advertised) polyacrylamide DR3046 is still efficient in sodium chloride brines, Figure 14 clearly shows the deleterious effect that the divalent

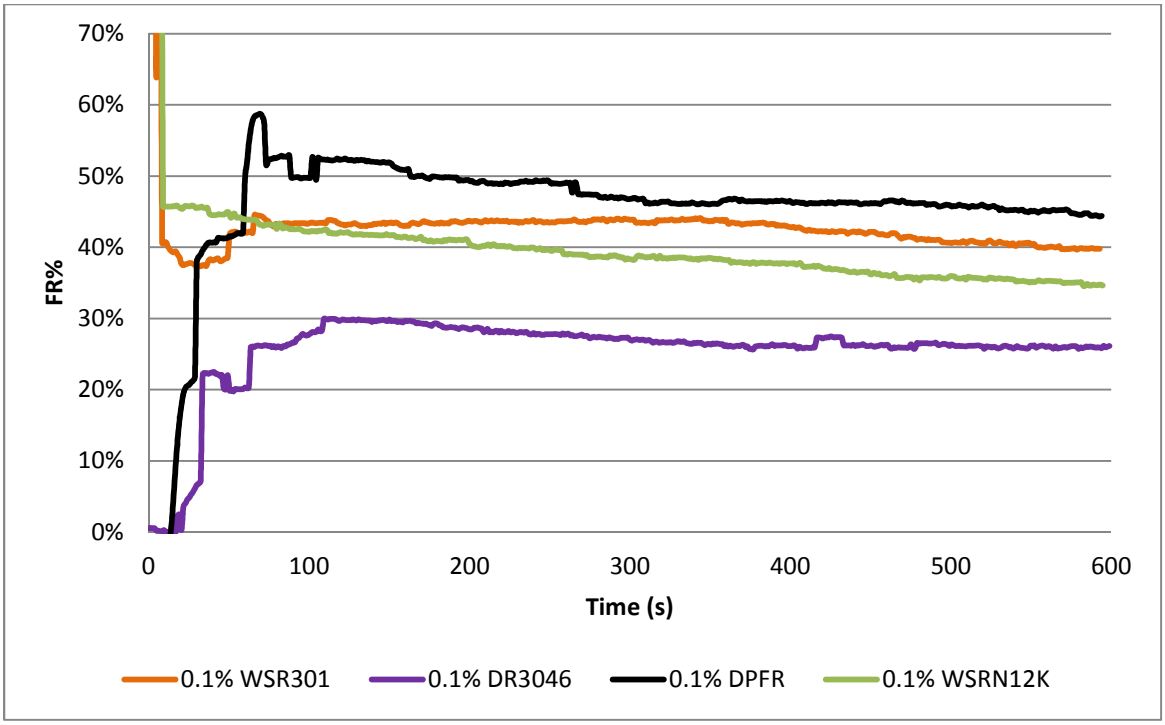

Figure 14 - Comparison of Friction Reducers (DR3046, DPFR, WSR301, WSRN12K) in 5% $CaCl_2$ at 0.1% Polymer Concentration

calcium ions have on its effectiveness. As mentioned in Chapter 2: Literature Review, it is widely accepted that divalent cations are the most troublesome for polyacrylamides in reused flowback water, and these experiments confirm this trend. As before, the PEO WSR301 and the novel DPFR are still comparable with each other, even though 5% $CaCl_2$ is almost twice the maximum concentration observed by Hayes in a study of Marcellus Shale flowback water (2011), and 10% $CaCl_2$ is far above most flowback waters' Ca^{2+} concentration. These high concentrations were chosen to attempt to find the limit of performance for the friction reducers. In 10% $CaCl_2$, it is clear that the typical friction reducer (DR3046) is not capable of maintaining the same level of performance as observed at lower Ca^{2+} and lower salt concentrations. Both the hydration/inversion time and maximum friction reduction percentage are inhibited.

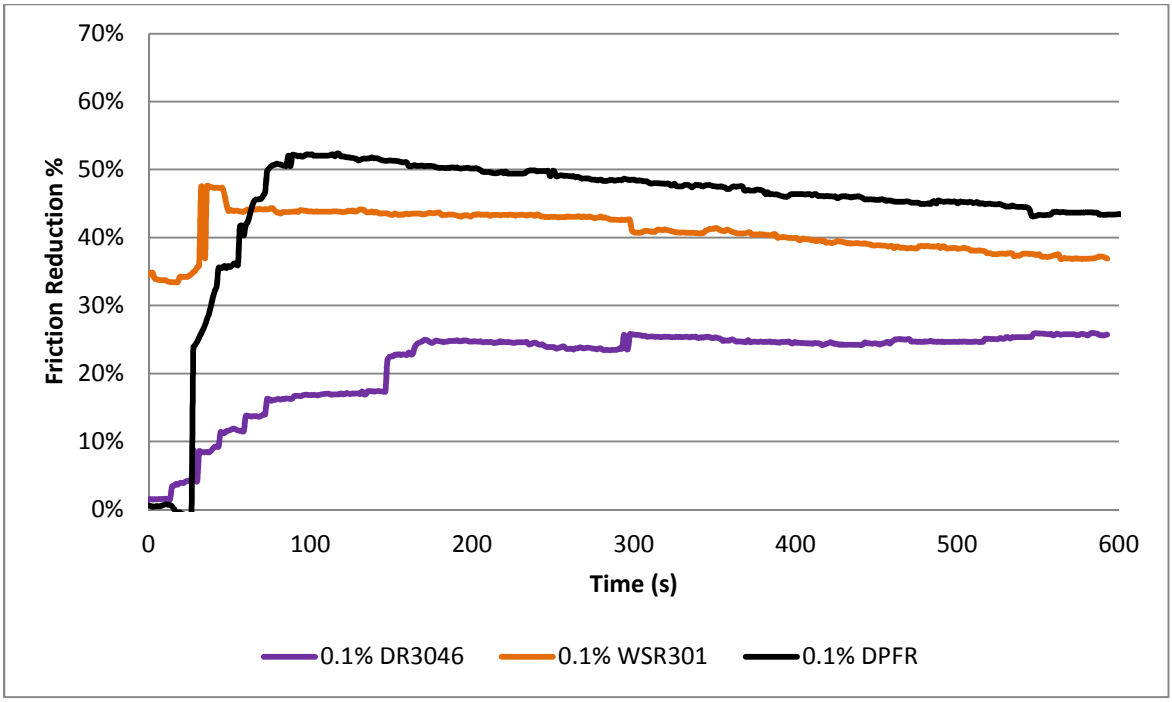

Figure 15 – Comparison of Friction Reducers (DR3046, DPFR, WSR301) in 10% $CaCl_2$at 0.1% Polymer Concentration

As a final comparison among the results from this series of experiments, the friction reduction percentages of the three friction reducers in a multisolute brine comprised of 7.4% NaCl and 1.76% $CaCl_2$ that simulates a flowback water that contains both mono- and divalent cations are shown in Figure 16. Here as in Figure 14, the PEO still performs the same as before in the other salt solutions, the novel DPFR is still the most efficient additive, and the typical DR3046 has a reduced maximum friction reduction and longer hydration time. These results are fairly similar to those found for other $CaCl_2$ brines because divalent cations are the controlling factor in decresasing friction reducer effectiveness.

After observing the three main friction reducers' effectiveness over time for each brine solution, it is useful to view a summary of these results to illustrate a few important

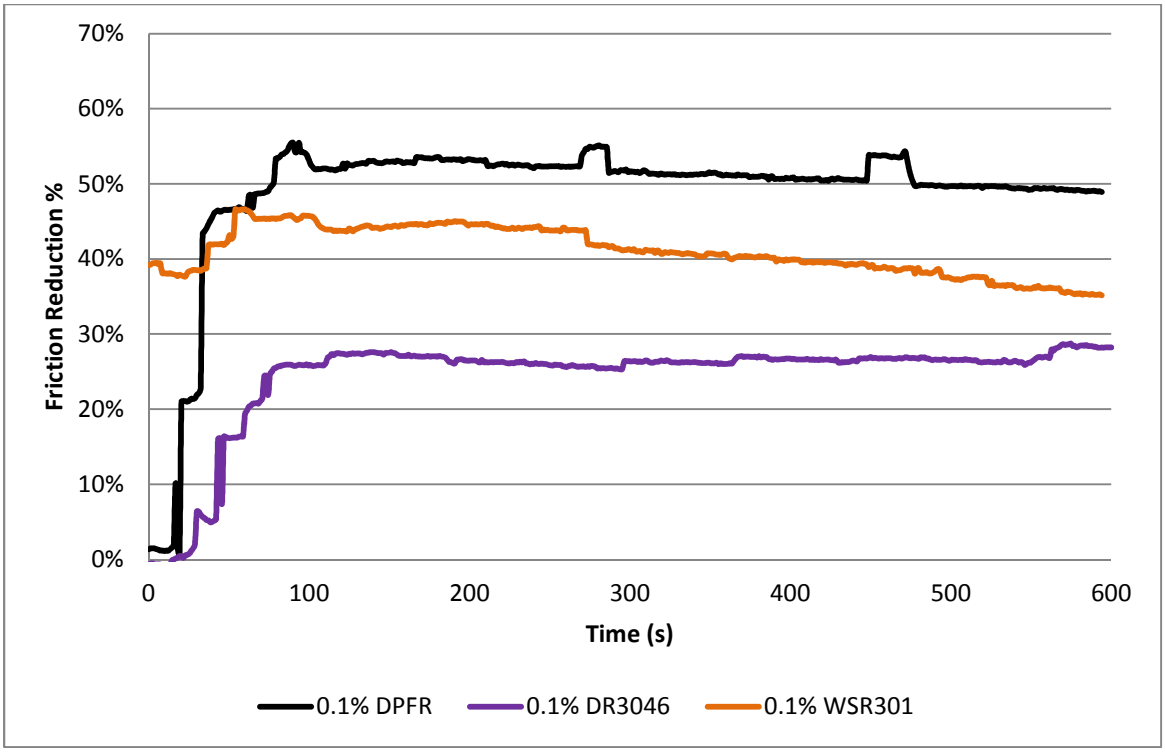

Figure 16 – Comparison of Friction Reducers (DR3046, DPFR, WSR301) in Multisolute Brine (7.4% NaCl, 1.76% $CaCl_2$) at 0.1% Polymer Concentration

trends. Both maximum and average friction reduction were calculated for all flow loop test runs, and the maximum values for the three main friction reducers are shown in Figure 17. First of all, the typical polyacrylamide DR3046 is comparably effective in pure water and 10% NaCl, but falters above this percentage and in any brine containing $CaCl_2$. Though this polymer is tailored for more saline water than normal polyacrylamides, it is still stored as most other friction reducers used in industry – as an inverse emulsion in oil. Because of this, there is more transformation that the friction reducer must go through to be fully activated: the additive must mix with the bulk solution (necessary for all concentrated additives), the emulsion must break or invert, and the now exposed polymers must hydrate to unfurl and disperse. One of the main factors in influencing hydration time could be the viscosity difference between the oil-based

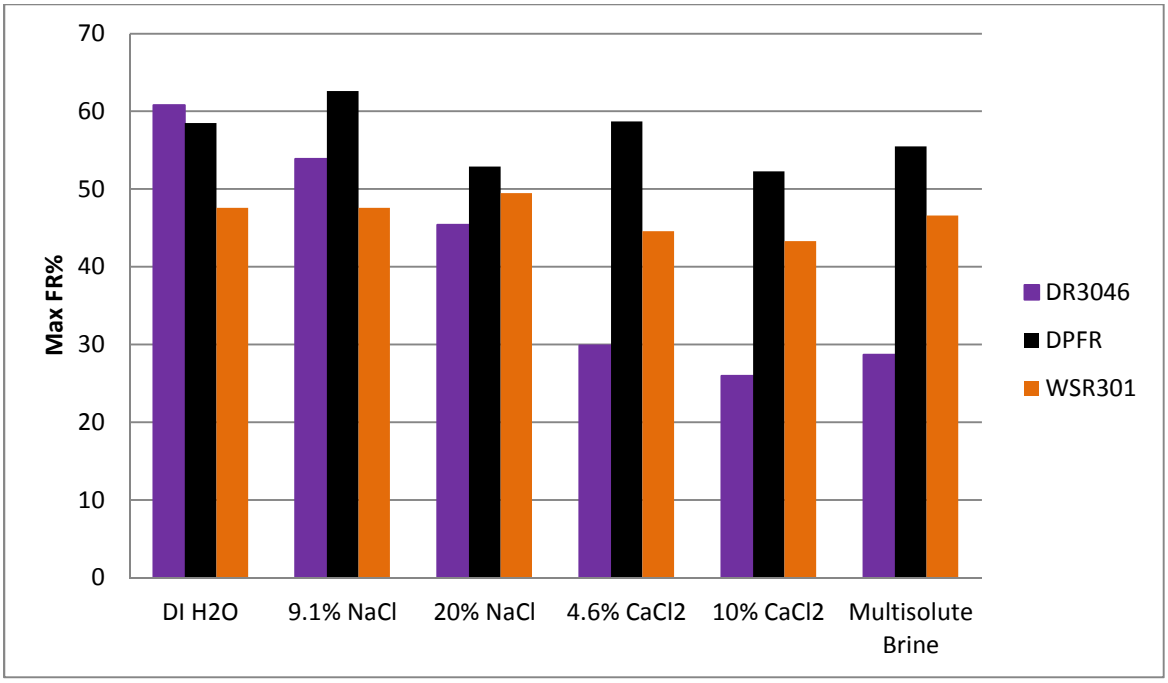

Figure 17 – Summary of Friction Reducers in Various Brines (WSR301 as Pre-Mixed Solution)

emulsion and the bulk brine (Zelenev, Gilzow, & Kaufman, 2009), which would explain why the DPFR hydrates more quickly. However, Figure 17 shows that it is also the maximum friction reduction of DR3046 that is affected. This is most likely due to the interference caused by the cations that prohibits polymer molecules from unfurling completely, thus diminishing their capacity to direct turbulent eddies' burst energies downstream in an anisotropic fashion. As expected, the DPFR performs strongly in any brine, though due to chemical research and development confidentiality, it can only be speculated as to exact cause of this.

The most interesting trend – or rather, lack thereof – in Figure 17 is the relative consistency of the performance of the PEO, WSR301, even though it was not quite as effective as DPFR. Though it was mentioned earlier that PEOs are not as strongly affected by salts as polyacrylamides (Sitaramaiah & Smith, 1969), we did not expect such

resistance to the high concentrations of NaCl and $CaCl_2$ the polymers were all subjected to. Though tests in even more concentrated brines were not conducted because flowback water encountered in the field is not as strong as what we have used, this data shows that PEOs possess and interesting advantage to polyacrylamides in that they could be used in a wide range of salt solutions without much need for optimization and chemical tailoring (as is done with polyacrylamides).

4.1.3 Optimization of PEO for friction reduction

From initial testing, polyethylene (PEO) solutions appeared to be quite resistant to changes in salt type and concentration across the various brine solutions tested, though those solutions did not perform as well as the novel polyacrylamide (DPFR) in all brines. The fact that PEO performance was independent of salt concentration outweighed the difference in performance between the two friction reducers, and continued testing of the PEO was warranted. The disadvantage of requiring pre-mixing of the solution still presented a hurdle to any useful field application. The majority of additives used in slickwater fracturing operations are added on-the-fly (i.e. continuously), reducing the need for static storage capacity of fresh water and base fluid on site, so an additive that is required to be batch-mixed prior to injection is not useful. As stated before, we determined that PEOs could be pre-dispersed in polypropylene glycol (PPG, MW=400) and then added to the base fluid as an on-the-fly additive. The proportion of PEO to PPG in the dispersion was first examined at 1:10 due to ease of preparation, then later at 1:5 to reduce the volume of PPG needed. These proportions equate to 0.1 wt% PEO in solution, with either 1 wt% or 0.5 wt% of PPG respectively. These dispersions were first tested in DI water to observe any differences in performance, as can be seen in Figure 18. The difference between these two dispersion proportions is negligible, and only noticeable

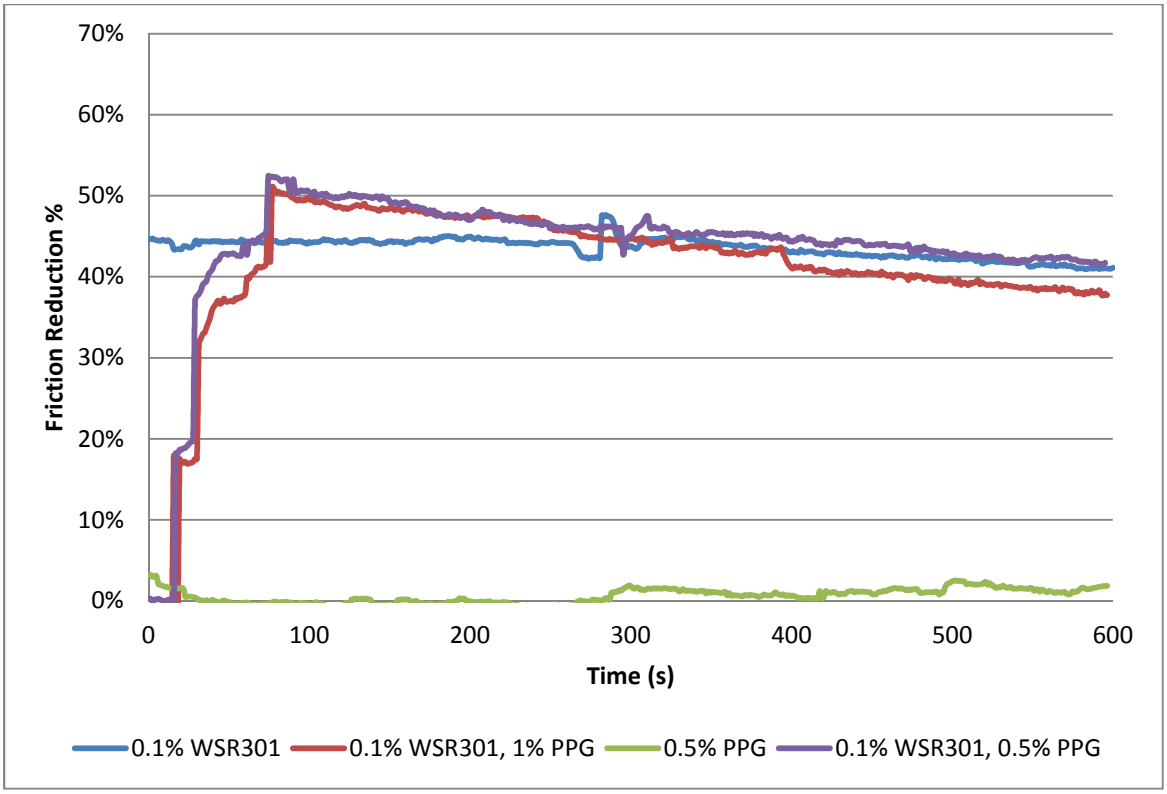

Figure 18 – Effects of Dispersing Agent on PEO Performance in DI Water

after about 400 seconds, where it appears that the 0.5% PPG solution degrades more. The pre-mixed PEO is also shown for comparison, and some interesting points can be seen. First, where the pre-mixed PEO solution starts at 45% friction reduction efficiency and degrades slightly after 400 seconds, the dispersions quickly rise to a clear maximum friction reduction percentage, just like a hydrating solution of polyacrylamide. Intrestingly, all PEO-containing solutions seem to converge on the same degradation slope after 300 to 400 seconds, indicating that perhaps there exists a buffering mechanism by which PEOs are protected from degradation until a certain condition is met. The third data series in Figure 18 is that of only 0.5% PPG in solution without any PEO, tested as a check to make sure that PPG does not have any friction reduction capability itself. Though this would be a normal check in any potentially synergistic system, PPG is

known to affect the cloud point temperature of a PEO solution, and it is a polymer as well (of much lower molecular weight), so there was extra reason to test any friction reduction potential of PPG.

Following the successful pre-dispersion of PEO in PPG (for a 0.5% solution), various salt solutions were tested to observe any differences in friction reduction percentage over time between pre-mixed PEO. If PPG can indeed improve the convenience and utility of PEO solutions, then it would be necessary that this does not also negatively impact friction reduction. Showing this comparison for each individual brine solution would be repetitive, since the effect is always the same as in DI water (Figure 18): the pre-mixed PEO starts around 45% friction reduction efficiency and starts to degrade around 400 seconds, while the dispersion quickly hydrates to a higher maximum friction reduction percentage but starts to degrade and eventually matches the slope of the corresponding pre-mixed test around 400 seconds. Instead, the comparisons for all brines are shown in Figure 19 as a comprehensive plot. Though quite complicated, this plot illustrates an important point: with little exception, the solutions with instantaneously added pre-dispersed PEOs perform nearly the same as their pre-mixed counterparts. Therefore, an on-the-fly version of this additive could be easily engineered with little change to the core properties and advantages of PEOs themselves. A bar graph form of this information (as in Figure 17) is shown in Figure 20.

Besides improving the utility and convenience of PEOs through pre-dispersion, the addition of urea was also briefly tested as a possible improvement to the system. As mentioned in Chapter 2: Literature Review, urea can be used as a “monomeric drag reduction enhancer” (Ahrenst, et al., 2008) as well as a complexing agent for improved shale stabilization downhole (Tadokoro, Yoshihara, Chatani, & Murahashi, 1964). To see if this potentially useful additive would affect the performance of the PEO dispersion, a

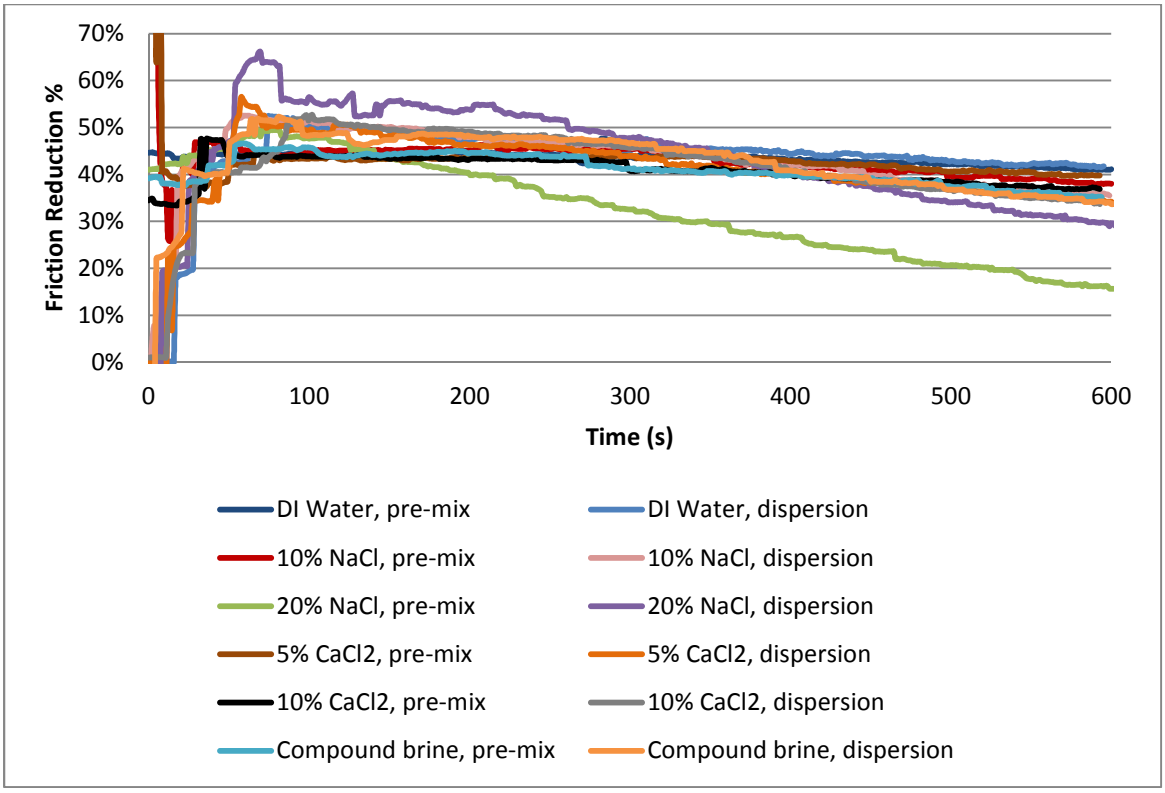

Figure 19 – Comparison of Pre-Mixed PEOs (WSR301 at 0.1%) and On-the-fly Addition (0.5% PPG Total)

base fluid of 1% urea in DI water was used as a fairly arbitrary starting point, then the dispersion of 0.1% WSR301 and 0.5% PPG was added as usual. The results of this test were surprising: the friction reduction of the solution was nearly the same as for the normal base fluid (simply DI water). Though it would seem intuitive at this point that PEOs are not affected significantly by additional additives, visual observation of the reservoir during the experiment revealed a large agglomeration (about 6 cm long) of what appeared to be PEO. Increased mixing of the reservoir briefly broke this up, but after the mixer was returned to normal speed the agglomeration reformed. While this was going on, the friction reduction remained unchanged and was still favorable, despite a sizeable proportion of the friction reducer itself trapped in an insoluble clump that could not travel

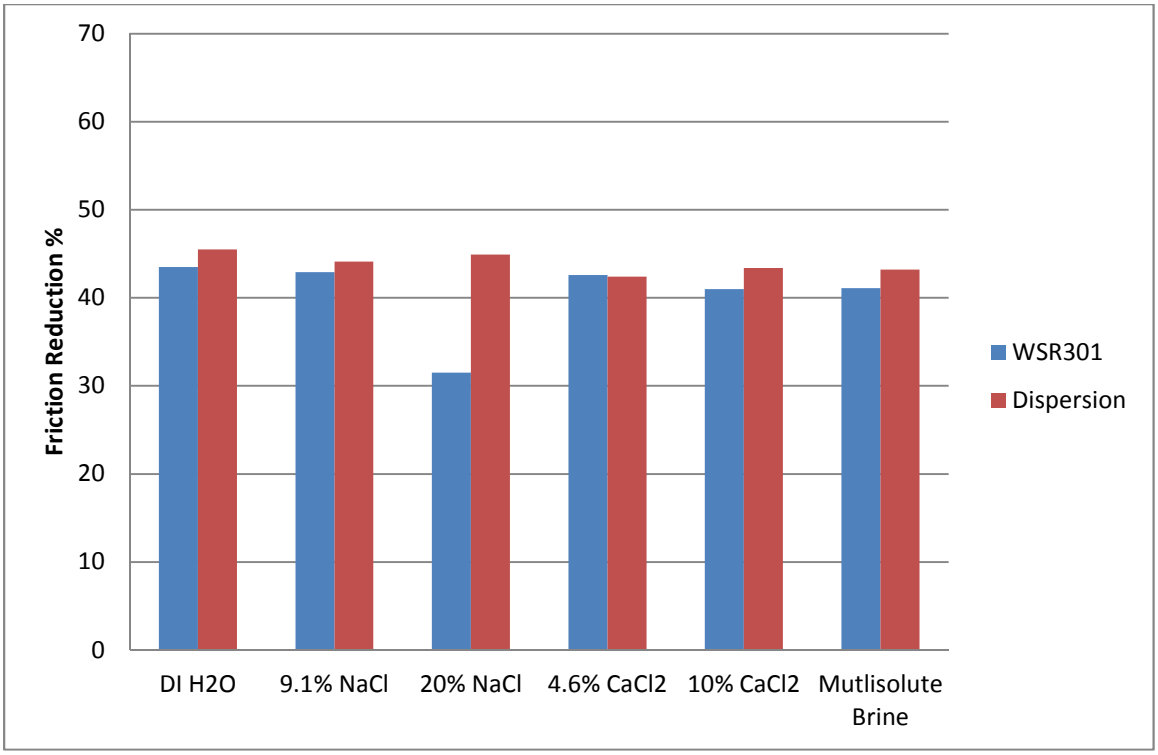

Figure 20 – Comparison of Pre-Mixed and Pre-Dispersed PEO (0.1% WSR301) in Various Brines

through the system. Figure 21 is a picture of the clump in the reservoir for reference. Since the results of the first experiment in 1% urea showed that the PEO would still reduce friction effectively even with most of it bound up in an unusable form, it was concluded that the small amount of PEO left in solution might still be effective because the urea allowed the molecules to agglomerate enough to reduce friction just as well as if the PEOs had been at a higher concentration. The possibility of reducing friction reducer concentration while still seeing the same effectiveness led to the next experiment: the same base fluid of 1% urea with only 10% of the PEO dispersion as before, so the concentrations of PEO and PPG were 0.01% and 0.05% respectively. Figure 22 shows the results of these experiments, along with a control test of 0.1% urea on its own to see if it reduced friction. As can be seen in the figure, the urea had very little effect on the full

Figure 21 – View of PEO-Urea Agglomeration During Testing of WSR301 Dispersion in 1% Urea

dispersion (0.1% PEO and 0.5% PPG), despite appearing to bind most of it in an unusable agglomeration. The results for the 10% dispersion are similar, though it seems that urea has a stronger effect on friction reduction since the PEO is not at a high enough concentration to still have a remaining soluble portion sufficient to cover the "critical concentration" needed for friction reduction. As expected, the urea has no effect on its own, but this is not because it acts independently: it is merely that the urea macroscopically binds up a portion of the PEO in solution, while possibly complexing (on a microscopic scale) the remaining dissolved PEO to enhance its friction reduction by increasing the effective molecular weight of each polymeric micelle. If urea turns out to

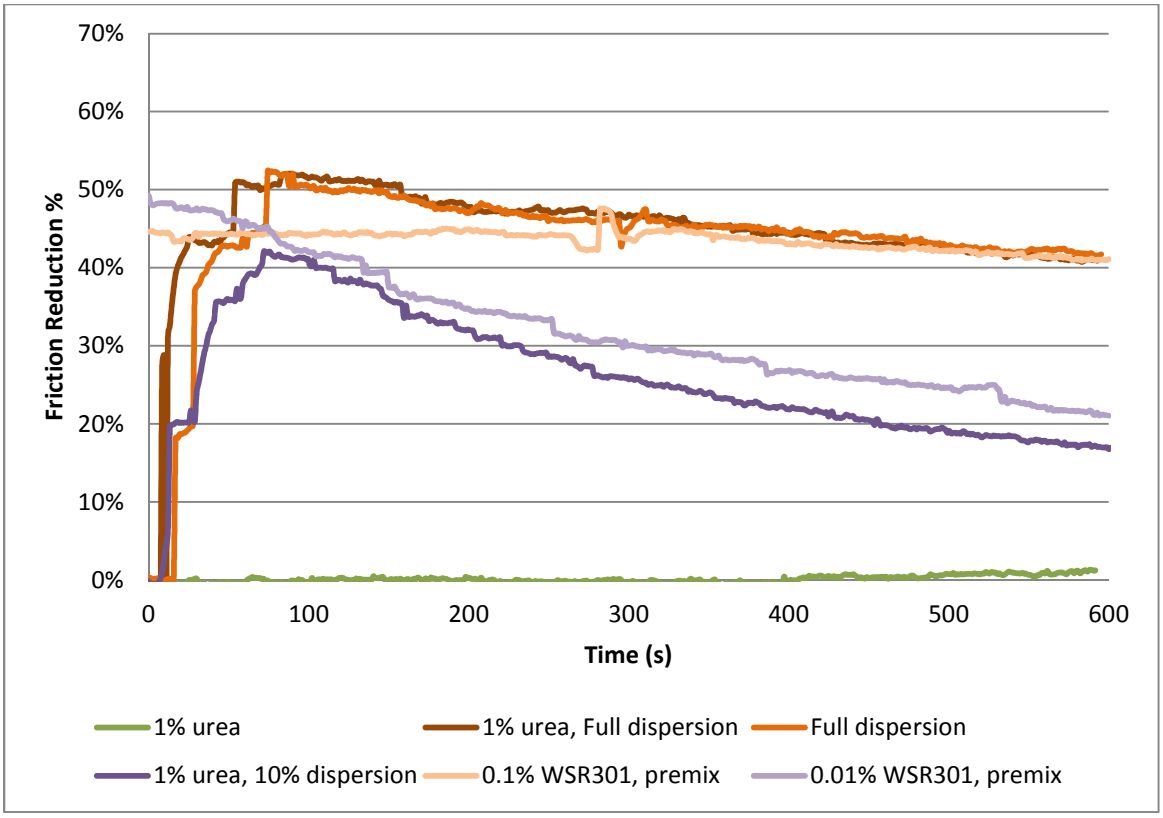

Figure 22 – Effects of Urea on 0.1% WSR301 Pre-Mixed and as a Dispersion. 10% Dispersion Refers to 0.01% WSR301 and 0.05% PPG

be an effective aid to shale stabilization by PEOs, then it can be added to a base fluid with minimal concern for drastic interference with the polymer.

In addition to the use of urea as an additive to the PEO-PPG system, the effect of heat on friction reduction in PEO solutions was tested, since the polymers are known to cloud out above a certain temperature and downhole conditions are often below this cloud point temperature (CPT). As mentioned before, a friction reducer must be soluble to be effective, and PEOs above the CPT gradually come further out of solution – therefore, one would expect the friction reduction performance of a PEO solution above its CPT to be comparably ineffective. Figure 23 shows two different high temperature test runs: the first is a PEO-salt system with a fairly low CPT of 40°C, and the second is

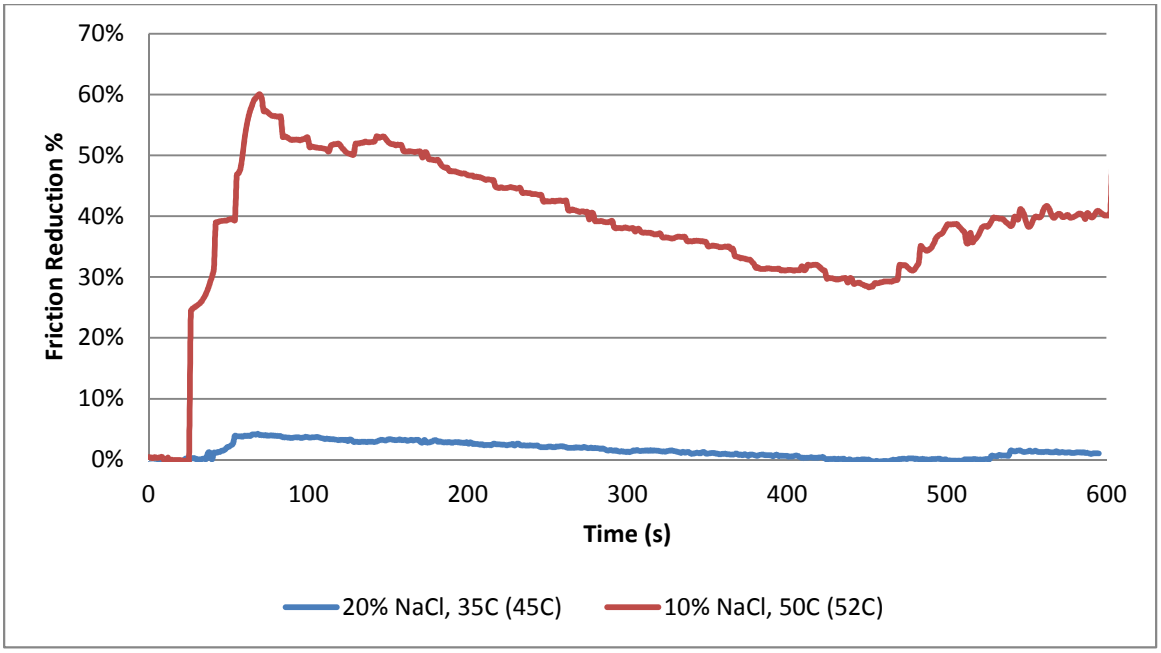

Figure 23 – Heated Tests for 0.1% WSR301 Dispersion

another system with a higher CPT of 59°C. The 10% NaCl test started with a very unusual baseline – normally the flow loop is operated at a consistent motor speed and a predictable pressure drop at a flow rate of 3 gpm is expected, but at 42°C the flow rate was already much higher than normal at a comparable motor speed (3.2 gpm versus 2.8 regularly), so a higher rate baseline was required in order to have room to decrease the motor speed in the possible event that the PEO actually reduces friction above its CPT. When the PEO dispersion was added to the heated base fluid, it dispersed but immediately clouded out, producing no friction reduction as can be seen in Figure 23. The second high temperature test – a higher CPT system of 10% NaCl and the PEO-PPG dispersion – produced even stranger results. The baseline again had to be much higher than normal at 3.5 gpm, while the test could only be run for about 8 minutes until the system started behaving strangely. At this point, the solution appeared to cloud out, even though the temperature had stayed constant and the system's CPT is at least 7°C above

the test temperature. This caused the flow rate to rapidly drop despite increasing the motor speed substantially in order to match the initial baseline flow rate. Figure 23 basically explains this graphically: the dispersion gives strong friction reduction immediately after addition, then dramatically degrades until the eight minute mark. The friction reduction percentage only rises here because the flow rate at those times was less than that used in the baseline (3.2 versus 3.5) with an increasing deficit – these values of friction reduction percentage are not valid because there was no corresponding baseline measurement to compare.

A final heated test produced another higher than expected baseline, and even more extreme results were observed, thereby confirming the inability to measure friction reduction of PEOs at temperatures near or above their cloud point.

4.2 DISCUSSION

The greatest discrepancy of the data presented in this thesis is that the maximum friction reduction percentages are not as high as reported in other studies. Often, polyacrylamides are measured at over 70%, including the DPFR tested in this research (Ferguson, Anderson, Eichelberger, Hallock, Qiu, & Roell, 2013), while PEOs have been measured at similar percentages at less than 100 ppm concentrations (Hoyt & Fabula, 1964). The likely reason for the former discrepancy is that the previously described flow loop in which these friction reducers were tested did not have as intense of turbulence as those used in industrial labs: our lab's flow loop has a calculated Re of 78,000 versus a high of 150,000 for a particular flow loop in the literature (Aften, Paktinat, & O'Neil, 2011). The discrepancy in PEO results can likely be attributed to the higher shear rate of our system versus ones used in the literature: a shear rate of over 20,000 s-1 was calculated for our system versus a high value of 17,000 s-1 for a comparable setup

(Paktinat, O'Neil, & Tulissi, 2011c). Since it is known that PEOs perform steadily worse when subjected to high shear rates, the comparatively small diameter of the pipe where friction pressure was measured could have contributed to a higher shear rate than PEOs had experienced at similar flow rates in literature studies using larger diameter pipes. The final flow loop (with ½" and 3/8" OD pipes instead of ¼" and ½"), is expected to produce even higher friction reduction percentage than seen in this report.

After observing the trends of the various tested friction reducers over a range of base fluid brines, a few conclusions arise. The first is that not all polyacrylamides that are advertised as salt-tolerant react in the same way to higher salt concentrations, as the two tested products showed: "high salt concentration" could refer to a brackish base fluid that has not been reused, or could refer to a salt solution near saturation. Another conclusion is that due to the consistent performance by both DPFR and PEOs in different brines, nearly any salt solution could be used for fracturing – not just flowback water. Finally, and perhaps the most interesting conclusion from this research, is that PEOs could find useful application in the hydraulic fracturing industry after virtually disappearing from the hydraulic fracturing literature for over 40 years.

The results of the novel and salt-tolerant DPFR are indicative of the intensive research that has been undertaken by chemical companies, oilfield service companies, and operators – the customizability of polyacrylamides and the need for using flowback water with high salt content has led to a wide array of specifically suited friction reducers adapted to a range of salt types and concentrations. This is why a sizeable body of literature since the late 2000s has been devoted to developing salt-tolerant polyacrylamides, many of which are referred to in the Polyacrylamides subsection of Chapter 2: Literature Review. As the DPFR performed strongly in even the most concentrated of solutions tested, it is highly recommended as a friction reducer for field

usage. The PEO also performed consistently well in every brine, either pre-mixed or when added as a dispersion in PPG on the fly. This means that both additives could be used by fracturing service companies in virtually any brine available: flowback water, produced water, or even non-oilfield sources such as rejected brine from desalination plants. The rejected brine from a high capacity reverse osmosis plant (RO) for treating sea water can contain up to 90,000 mg/L total dissolved solids (TDS, a proxy for salt concentration in brines) (Talavera & Ruiz, 2001), which is not even as concentrated as some of the produced waters in the Marcellus shale, which can reach levels above 120,000 mg/L TDS (Blauch, Myers, Moore, & Lipinski, 2009). Additionally, RO brine waste is virtually free of other contaminants and is a waste product that is becoming more expensive to dispose of – that is, it would essentially be a free source of water if it were to be utilized. Employing either the DPFR or PEOs to enable reuse of these difficult-to-treat water sources would solve multiple problems: how to dispose of brine waste, where to source water for hydraulic fracturing operations from, and how to deal with the negative interference of ions on traditional friction reducers.

Though the DPFR consistently performed the strongest in all brines tested, using PEOs could be a viable alternative to this additive for a few reasons. First of all, the DPFR is a novel and proprietary chemical that – although eminently suitable for fracturing operations around the world – might see limited usage outside of the North American market due to cost and availability constraints. Market information on this product is not published, but it is likely that, as it is essentially the "gold standard" of salt-tolerant friction reducers, may command a price premium that smaller service companies would not be able to afford. PEOs, on the other hand, have been produced for at least 80 years (not always by the same company, due to acquisitions and mergers), and are likely less expensive due to their simpler composition and long-standardized

synthesis. Additionally, the polymers are sold as a solid, allowing for easy transport and long term storage. The flexibility in usage affords an advantage to the user as well: a wide range of molecular weights (encompassing at least four grades) can be used with similar effect, and a range of usable concentrations (centered around 1 ppt) allow for flexibility and a greater tolerance for operator error. Though optimization of the PEO-PPG dispersion additive would require more progress before commercialization, it is possible to mix different grades of PEO in various concentrations to take advantage of the differing properties of the different MW polymers. For example, lower MW PEOs or polyethylene glycols have the potential to stabilize shale but are only mediocre friction reducers, while high MW PEOs are excellent friction reducers but are not able to enter shale pores in order to stabilize the formation – a combination of the two could provide the benefits of both grades.

Using PEOs as friction reducers is not without disadvantages, mostly due to the lack of research relative to application in hydraulic fracturing. First of all, though both PEO and polyacrylamide are nontoxic polymers, the high temperatures encountered in shale formations could cause decomposition of polymers into more toxic residues, leaving open the issue of environmental fate and transport. According to Carman and Cawiezel, polyacrylamides are stable up to 200°C, which is much higher than typical shale formations; when they do degrade, it is not into its carcinogenic acrylamide monomer (2007). At lower temperatures, it can only be broken by oxidative breakers, which are usually pumped as part of a fracture operation. PEOs are also thermally stable, and only start breaking down under pyrolysis conditions at about 320°C, at which point the polymers break down into easily degradable compounds such as formaldehyde, ethanol, carbon dioxide, and water (Madorsky & Straus, 1959). Since neither polymer is likely to break down with high formation temperatures other than by oxidative breaker

addition, it is important to ensure the nontoxicity of the polymers themselves: polyacrylamides are currently used in cosmetic surgery as fillers that integrate into tissue (Contura International A/S, 2013), while PEOs are used for drug delivery systems as capsule coatings (Dow Chemical Company, 2002). Therefore, the potential environmental impact of these friction reducers is expected to be low.

With toxicity apparently a non-issue, the other unknown factor that must be addressed is the ability of PEOs to stabilize shale. Shale stabilization tests with both PEOs and polyacrylamides are currently being run to test the abilities of both to prevent water intrusion and subsequent swelling of reactive shales using both hot rolling oven and fracture conductivity tests (Mimouni, 2014). The results so far indicate that PEO is excellent at stabilizing shale particles, but may need further optimization in order to minimize impacts on fracture conductivity. Additionally, the urea formulations tested in the flow loop could be an improvement to the shale stabilization afforded by PEOs alone.

Chapter 5: Conclusions

5.1 SUMMARY

This research involved testing friction reducers – a typical polyacrylamide, a novel salt-tolerant polyacrylamide, and polyethylene oxide (PEO) – in a flow loop that was designed and constructed for this purpose. The results show that, though the novel-salt tolerant polyacrylamide (DPFR) was the strongest performer in a wide range of NaCl and $CaCl_2$ brine concentrations, the consistent and salt-independent performance of PEOs could present a new solution for friction reduction in hydraulic fracturing operations. The PEOs are likely to be cheaper, more widely available, and require less demanding design and mixing protocols than specially designed polyacrylamides, and therefore could find utilization in shale plays that need to recycle flowback and produced water at minimal cost and treatment effort. In addition to allowing oilfield sources of water to be used in subsequent fracturing operations with no removal of salt ions, nontraditional sources could be effectively utilized, including rejected brine from reverse osmosis plants and seawater.

Overall, the results shown represent a potential for major change in the hydraulic fracturing industry. If it turns out that PEO solutions not only reduce friction effectively with any type of brine but also stabilize shale due to the presence of high salt concentrations and the clouding effect of the polymers, then potential exists for their widespread use in fracturing. Multifunctional additives generally only find limited use in fracturing (when compared to drilling, for example), but the possibility of performing three functions – friction reduction, shale stabilization, proppant suspending – could allow for reduction in additive usage, operating costs and risk of environmental contamination.

5.2 LIMITATIONS

Though the flow loop testing produced consistent results with readily observable trends, future testing should be performed using the updated design of the flow loop in order to reduce shear while increasing the Reynolds number. This should produce results similar to those obtained from larger flow loops. Ideally, after optimization of a certain PEO or polyacrylamide additive-brine system, field-scale testing in oilfield-size pipes is recommended, since it is known that scaling friction reduction results is challenging (Sellin & Ollis, 1983).

More importantly, however, the greatest limitation to testing the suitability of friction reducers with respect for use in recycled flowback waters was the lack of available actual flowback water samples in this research. Testing with actual flowback water as well as more complex synthetic brines should be conducted in the future. These experiments would evaluate potential interferences from other expected contaminants such as bacteria and their enzymes, returned frac chemicals, particulates, and any oil-phase residues. Nevertheless, the multisolute brine used in testing was considered representative of the two most prevalent cations in typical flowback brine (sodium and calcium), while other species are often present at concentrations that are orders of magnitude less than these.

5.3 FUTURE WORK

The first order of business – to be completed soon after the release of this thesis, in fact – will be to finish construction of the aforementioned larger and improved flow loop. With all improvements in place, this should give higher friction reduction percentage results for the various additives, as well as more accurate results due to the measurement and control of the pump's flow rate to ensure a constant level.

In addition to mechanical testing, chemical testing of the degradation of PEOs downhole is highly recommended, since at present the literature available on PEO destruction revolves around pyrolysis, shear degradation, and even wet-air oxidation in industrial wastewater treatment (Mantzavinos, Livingston, Hellenbrand, & Metcalfe, 1996). Pyrolysis experiments generally do not include water, so this would be an interesting factor to consider since hydrolytic degradation could be a prominent depolymerization mechanism.

Though optimization of most polyacrylamides in various brines is performed in-house by the chemical developers, PEOs have only recently begun to be optimized for hydraulic fracturing usage (Dow Chemical Company, 2014). Therefore, creating a more comprehensive test matrix of various brines (both single-salt and compound brines), flowback and produced water, and varying the concentration, molecular weight, and blend of PEOs would provide a more complete picture of the polymers' potential. All these experiments should be performed with the PEO-PPG dispersion, since even in this early stage it is a much more convenient and realistic method of adding the chemicals. The dispersion itself also will require further optimization, since it is not currently stable in its current formulation.

The prospect of using urea as either a monomeric friction reduction aid or a complexing agent for shale stabilization is another potential area of further research, though this direction will highly depend on the performance of PEOs in fracture conductivity tests.

If, after larger scale flow loop testing and dispersion optimization, field testing is proposed, proper equipment would need to be used for this application. It is already an established practice of preparing a guar dispersion in diesel fuel or other nonpolar dispersant for continuous addition to water in order to avoid clumping of the guar powder

in water. The PEO-PPG dispersion could be prepared in similar batch mixers and agitated during a brief storage time before it is blended with the fracturing base fluid using an additive pump (which would have to be a progressive cavity pump). Fortunately, this means that no additional equipment would need to be developed or purchased by a typical service company.

In conclusion, though this research represents the initial development for a promising new multifunctional fracturing additive, much work remains for further optimization or even field-testing of the friction reducers.

Appendix A: Criteria for Flow Loop Design from Literature

Reservoir volume	Length of pressure drop	Pipe ID	Flow Rate	FR used	FR concentration	Brine types	Researcher
30 L	1 m	0.42”	1.5 to 5 gpm	PHPA	0.000313 to 0.0025 (v/v)	Fresh water	Ercan and Ozbayoglu, 2009
60 L	3 m (3 sections)	5/8”, ½” 3/8”	12 gpm	Standard cationic, standard anionic,	0.03 to 0.12%	Surface water, 7% NaCl,	Paktinat et al, 2011 (x2)
20 L	N/A	0.5”	24 gpm	11 anionic, 1 cationic, 1 nonionic	0.05 to 1 gpt	Fresh water, 2% KCl, 15%	Aften 2010
150 gal	N/A	0.435”	3 to 21 gpm	“powdered, high MW”	0.02 to 0.1 lb/bbl	Fresh water, 7% KCl, 10 ppg	Fox et al, 2008
42 gal	10 ft	1”	50 gpm	“new”	0.25 and 0.5 gpt	Fresh water, 2% KCl, 10%	Sun et al, 2011
N/A	5 ft	1/8”	1 to 20 gpm	Polyhall 654 and 603 (polyacrylamides)	1,3 and 8 gpt	Distilled water, tap water,	Sitaramaiah and Smith, 1969

Range of Reynolds numbers: 75,000 to 150,000
Range of shear rates: 3800 to 17,000 s^{-1}

Appendix B: First Flow Loop

The original design of the flow loop was constructed from readily available parts, and was not capable of reaching a Reynolds number over 4000. It was soon realized that this setup did not allow significant friction reduction to occur due to the fluid remaining in the laminar flow regime. As can be seen in Figure 24, the phenomenon of friction reduction in a dilute polymer solution (i.e. decrease in Fanning friction factor *f*) is only observed at Re values above 4000, and becomes more pronounced with more turbulent flow. Before designing a new flow loop to produce sufficient turbulent flow, I tested the three friction reducers to establish concentrations to be used for future tests, and found

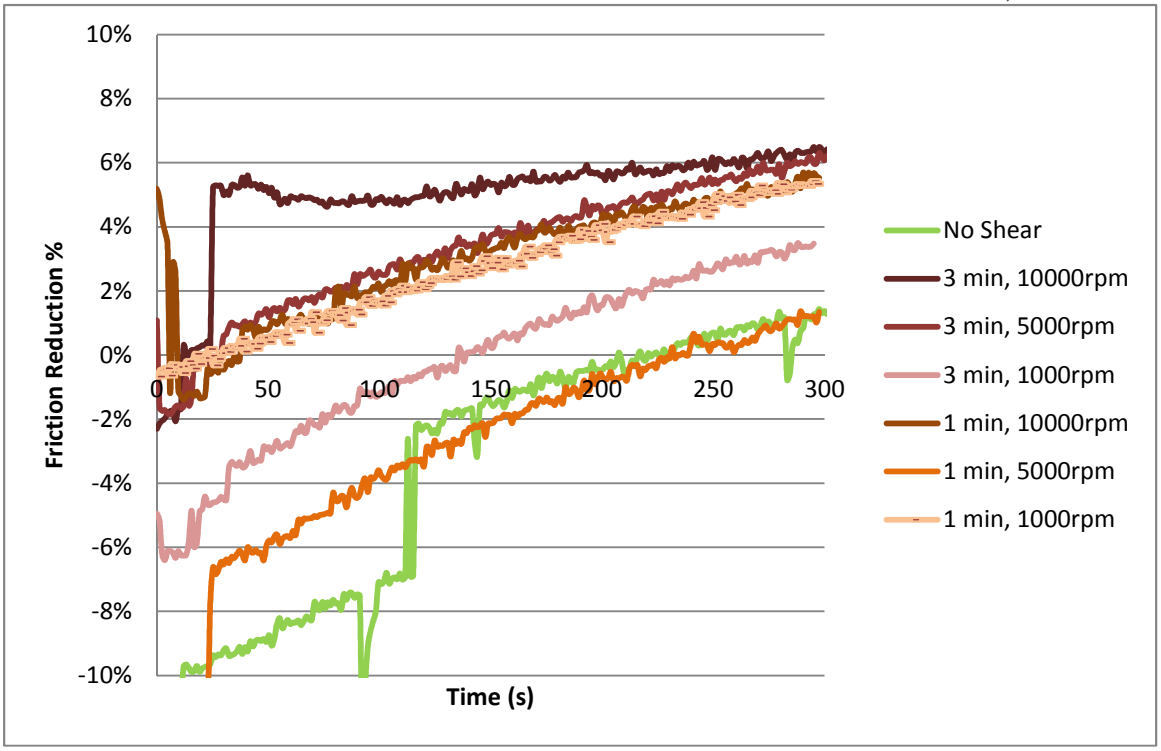

Figure 24 - FR% as Function of Shear History (RPM and Time Variation)

after a few runs that the emulsified polyacrylamide (DR3046) was not able to invert and hydrate without sufficient shear and turbulence. Using an OFITE blender to pre-shear the

solutions, further tests confirmed this requirement of shear- and turbulence-activated friction reduction, as seen in Figure 24. The optimum shear history of the DR3046 was chosen as 8000 rpm for 3 minutes after further testing. This preparation was used when testing the solutions' shale stabilization properties. The testing of PEOs in this system was similarly unfruitful, primarily since the slippage of gears in the positive displacement gear pump very quickly degraded the solutions to the point of not reducing friction at all. Therefore, FR% was essentially zero for any PEO solutions tested. Furthermore, after noting the predicted onset of friction reduction value of Re*f1/2 according to the work of Virk (1975), it appears that the value in this flow loop would have been around 950, which is smaller than the estimated required 1100 needed for any observable friction reduction in a solution of high-MW PEO at 0.1% concentration by mass.

Bibliography

Aften, C. W., & Watson, W. P. (2009). Improved Friction Reducer for Hydraulic Fracturing. Society of Petroleum Engineers 118747. The Woodlands, TX: Society of Petroleum Engineers.

Aften, C., Paktinat, J., & O'Neil, B. (2011). Critical Evaluation of Biocide-Friction Reducer Interactions Used in Slickwater Fracs. Society of Petroleum Engineers 141358. The Woodlands, TX: Society of Petroleum Engineers.

Ahrenst, A., Lungwitz, B., Fredd, C. N., Abad, C., Gurmen, N., Chen, Y., et al. (2008, March 13). Patent No. 11/833,449. United States of America.

Alramahi, B., & Sundberg, M. I. (2012). Proppant Embedment and Conductivity of Hydraulic Fractures in Shales. 46th US Rock Mechanics/Geomechanics Symposium, 12-291. Chicago, IL: American Rock Mechanics Association.

Bland, R., Smith, G. R., Eagark, P., van Oort, E., & Dharma, N. (1996). Low Salinity Polyglycol Water-Based Drilling Fluids as Alternatives to Oil-Based Muds. Society of Petroleum Engineers 36400. Kuala Lumpur, Malaysia: Society of Petroleum Engineers.

Blauch, M. E. (2010). Developing Effective and Environmentally Suitable Fracturing Fluids Using Hydraulic Fracturing Flowback Waters. Society of Petroleum Engineers 131784. Pittsburgh, PA: Society of Petroleum Engineers.

Blauch, M. E., Myers, R. R., Moore, T. R., & Lipinski, B. A. (2009). Marcellus Shale Post-Frac Flowback Waters - Where is All the Salt Coming From and What Are the Implications? Society of Petroleum Engineers 125740. Charleston, WV: Society of Petroleum Engineers.

Calahorra, E., Cortazar, M., & Guzman, G. M. (1985). Thermal Decomposition of Poly(ethylene Oxide), Poly(methyl Methacrylate) and Their Mixtures by Thermogravimetric Method. Journal of Polymer Science: Polymer Letters Edition, 23, 257-260.

Carman, P. S., & Cawiezel, K. E. (2007). Successful Breaker Optimization for Polyacrylamide Friction Reducers Used in Hydraulic Fracturing. Society of Petroleum Engineers 106162. College Station, TX: Socieity of Petroleum Engineers.

Colebrook, C. F. (1939). Turbulent Flow in Pipes, with Specific Reference to the Transition Region between the Smooth and Rough Pipe Laws. Journal of the ICE, 11(4), 133-156.

Contura International A/S. (2013). About Aquamid. Retrieved April 22, 2014, from Aquamid: Your Beauty Secret to Keep: http://www.aquamid.com/consumer/about-aquamid/harmony

Den Toonder, J. M., Hulsen, M. A., Kuiken, G. D., & Nieuwstadt, F. T. (1997). Drag Reduction by Polymer Additives in a Turbulent Pipe Flow. Journal of Fluid Mechanics, 337, 193-231.

Dow Chemical Company. (2002). Polymer Resources. Retrieved 2013, from Dow Corporate Web Site: http://www.dow.com/scripts/litorder.asp?filepath=/pdfs/noreg/326-00001.pdf&pdf=true

Dow Chemical Company. (2013, December 11). POLYOX Solution Preparation - Predispersion in Water-Miscible Non-Solvents. Retrieved 2013, from Dow Wolff Cellulosics: http://dowwolff.custhelp.com/app/answers/detail/a_id/1375/kw/1375

Dow Chemical Company. (2014). Polyslip OF-50 Polymer. Retrieved April 29, 2014, from Dow Wolff Cellulosics: http://www.dow.com/webapps/include/getdoc.aspx?objectid=&filepath=polyox/pdfs/noreg/787-00008.pdf&pdf=true

Downs, J. D., van Oort, E., Redman, D. I., & Ripley, D. (1993). TAME: A New Concept in Water-Based Drilling Fluids for Shales. Society of Petroleum Engineers 26699. Aberdeen, UK: Society of Petroleum Engineers.

Ercan, C., & Ozbayoglu, M. E. (2009). "PHPA" as a Frictional Pressure Loss Reducer and its Pressure Loss Estimation. Society of Petroleum Engineers 125992. Manama, Bahrain: Society of Petroleum Engineers.

Ferguson, M. L., Anderson, C. C., Eichelberger, P. B., Hallock, J. K., Qiu, X., & Roell, R. L. (2013). Innovative Friction Reducer Improves Performance and Greater Flexibility in Recycling Highly Mineralized Produced Brines. Society of Petroleum Engineers 164535. The Woodlands, TX: Society of Petroleum Engineers.

Florin, E., Kjellander, R., & Eriksson, J. C. (1984). Salt Effects on the Cloud Point of Poly(ethylene oxide)+Water System. Journal of the Chemical Society, Faraday Transactions 1, 80, 2889-2910.

Fox, K. B., Stouffer, C. E., & Utley, B. (2008). Evaluation of a New Friction Reducer for Brines. AADE Fluids Conference and Exhibition. Houston, TX: American Association of Drilling Engineers.

Gordon, R. J. (1970). On the Explanation and Correlation of Turbulent Drag Reduction in Macromolecular Solutions. Journal of Applied Polymer Science, 14, 2097-2105.

Grubert, E. A., Beach, F. C., & Webber, M. E. (2012). Can Switching Fuels Save Water? A Life Cycle Quantification of Freshwater Consumption for Texas Coal- and Natural Gas-Fired Electricity. Environmental Research Letters, 1-11.

Hamouda, A. A., & Omotayo, M. T. (2007). Effect of Temperature on Degradation of Polymer Drag Reduction and Heat Transfer in Non-Newtonian Fluid. Society of Petroleum Engineers 106081. Houston, TX: Society of Petroleum Engineers.

Hayes, T. (2011). Characterization of Marcellus and Barnett Shale Flowback Waters and Technology Development for Water Reuse. Hydraulic Fracturing Technical Workshop #4. Arlington, VA: GTI.

Hightower, M. (2011). Energy Meets Water. Mechanical Engineering, 34-39.

Horn, A. D. (2009). Breakthrough Mobile Water Treatment Converts 75% of Fracturing Flowback Fluid to Fresh Water and Lowers CO2 Emissions. Society of Petroleum Engineers 121104. San Antonio, TX: Society of Petroleum Engineers.

Howarth, R. W., Ingraffea, A., & Engelder, T. (2011). Should Fracking Stop? Nature, 271-275.

Hoyt, J. W. (1972, June). The Effect of Additives on Fluid Friction. Transcation of the ASME: Journal of Basic Engineering, 94(2), 258-285.

Hoyt, J. W., & Fabula, A. G. (1964). The Effect of Additives on Fluid Friction. Fifth Symposium on Naval Hydrodynamics, Ship Motions, and Drag Reduction, (pp. 947-974). Bergen, Norway.

Jenkins, S. (2012). Frac Water Reuse. Chemical Engineering, 14-16.

Ke, M., Qu, Q., Stevens, R. F., Bracksieck, N., Price, C., & Copeland, D. (2006). Evaluation of Friction Reducers for High-Density Brines and their Application in Coiled Tubing at High Temperatures. Society of Petroleum Engineers103037. San Antonio, TX: Society of Petroleum Engineers.

Kjellander, R., & Florin, E. (1981). Water Structure and Changes in Thermal Stability of the System Poly(ethylene Oxide) – Water. Journal of Chemical Science, Faraday Transactions 1, 77, 2053-2077.

Li, L., Ezeokonkwo, C. I., Lin, L., Eliseeva, K., Kallio, W., Boney, C. L., et al. (2010). Well Treatment Fluids Prepared with Oilfield Produced Water: Part II. Society of Petroleum Engineers 133379. Florence, Italy: Society of Petroleum Engineers.

Lindsay, S. D., McNeil, F., Sackash, M. J., & Bryant, J. E. (2011). Use of Salt-Tolerant Friction Reducer for Coiled-Tubing Applications in Unconventional Shale Formations. Society of Petroleum Engineers 142064. The Woodlands, TX: Society of Petroleum Engineers.

Madorsky, S. L., & Straus, S. (1959). Thermal Degradation of Polyethylene Oxide and Polypropylene Oxide. Journal of Polymer Science, 36, 183-194.

Mantzavinos, D., Livingston, A. G., Hellenbrand, R., & Metcalfe, I. S. (1996). Wet Air Oxidation of Polyethylen Glycoles; Mechanisms, Intermediates and Implications for Integrated Chemical-Biological Wastewater Treatment. Chemical Engineering Science, 51(18), 4219-4235.

Mimouni, A. S. (2014). Master's Thesis. Master's Thesis, Austin, TX.

Nouri, H. H., & Root, P. J. (1971). A Study of Polymer Solution Rheology, Flow Behavior, and Oil Displacement Processes. Society of Petroleum Engineers 3523. New Orleans, LA: American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.

Paktinat, J., O'Neil, B., & Tulissi, M. (2011b). Case Studies: Improved Performance of High Brine Friction Reducers in Fracturing Shale Reservoirs. Society of Petroleum Engineers 148794. Columbus, OH: Society of Petroleum Engineers.

Paktinat, J., O'Neil, B., & Tulissi, M. (2011c). Case Studies: Impact of High Salt Tolerant Friction Reducers on Fresh Water Conservation in Canadian Shale Fracturing Treatments. Society of Petroleum Engineers 149272. Calgary, Alberta: Society of Petroleum Engineers.

Paktinat, J., O'Neil, B., Aften, C., & Hurd, M. (2011). High Brine Tolerant Polymer Improves the Performance of Slickwater Frac in Shale Reservoirs. Society of Petroleum Engineers 144210. The Woodlands, TX: Society of Petroleum Engineers.

Papso, J., Blauch, M., & Grottenthaler, D. (2010). Cabot Gas Well Treated with 100% Reused Frac Fluid. Indiana, PA: Superior Well Services.

Paterson, R. W., & Abernathy, F. H. (1970). Turbulent Flow Drag Reduction and Degradation with Dilute Polymer Solutions. Journal of Fluid Mechanics, 43(4), 689-710.

Pedlow, J. W. (2013). A Study of the Effect of Stress and Fluid Sensitivity on Propped Fracture Conductivity in Preserved Reservoir Shales. University of Texas at Austin, Petroleum and Geosystems Engineering. Austin, TX: University of Texas at Austin.

Pruitt, G. T., Rosen, B., & Crawford, H. R. (1966). Effect of Polymer Coiling on Drag Reduction. Research Division. Dallas, TX: The Western Company.

Puder, M. G., & Veil, J. A. (2007). Options, Methods, and Costs for Offsite Commercial Disposal of Oil and Gas Exploration and Production Wastes. Society of Petroleum Engineers 105178. Galveston, TX: Society of Petroleum Engineers.

Rimassa, S. M., Howard, P. R., & Blow, K. A. (2009). Optimizing Fracturing Fluids from Flowback Water. Society of Petroleum Engineers 125336. San Antonio, TX: Society of Petroleum Engineers.

Robb, I. D., Welton, T. D., Bryant, J., & Carter, M. L. (2010, December 7). Patent No. 7,846,878 B2. United States of America.

Savins, J. G. (1964). Drag Reduction Characteristics of Solutions of Macromolecules in Turbulent Pipe Flow. Society of Petroleum Engineers Journal, 203-214.

Savins, J. G. (1966). A Stress-Controlled Mechanism Drag-Reduction Phenomenon. Society of Petroleum Engineers 1724. Houston, TX: American Institute of Mining, Metallurgical, and Petroleum Engineers.

Schein, G. (2005). The Application and Technology of Slickwater Fracturing. Society of Petroleum Engineers Distinguished Lecture. Society of Petroleum Engineers.

Sellin, R. H., & Ollis, M. (1983). Effect of Pipe Diameter on Polymer Drag Reduction. Industrial & Engineering Chemistry Product Research and Development, 22(3), 445-452.

Sellin, R. H., Hoyt, J. W., Poliert, J., & Scrivener, O. (1982). The Effect of Drag Reducing Additives on Fluid Flows and Their Industrial Applications Part 2: Present Applications and Future Proposals. Journal of Hydraulic Research, 20(3), 235-292.

Shenoy, A. V. (1984). A Review on Drag Reduction with Special Reference to Micellar Systems. Colloid and Polymer Science, 262, 319-337.

Shetty, A. M., & Solomon, M. J. (2009). Aggregation in Dilute Solutions of High Molar Mass Poly(ethylene) Oxide and its Effect on Polymer Turbulent Drag Reduction. Polymer, 50, 261-270.

Sitaramaiah, G., & Smith, C. L. (1969). Turbulent Drag Reduction by Polyacrylamide and Other Polymers. Society of Petroleum Engineers Journal, 9(2), 183-188.

Sun, H., Wood, B., Stevens, D., Cutler, J., Qu, Q., & Lu, M. (2011). A Nondamaging Friction Reducer for Slickwater Frac Applications. Society of Petroleum Engineers 139480. The Woodlands, TX: Society of Petroleum Engineers.

Tadokoro, H., Yoshihara, T., Chatani, Y., & Murahashi, S. (1964). A Preliminary Report of Structural Studies on Polyethylene Oxide-Urea Complex. Journal of Polymer Science Part B: Polymer Letters, 2(4), 363-368.

Talavera, J. L., & Ruiz, J. J. (2001). Identification of the Mixing Processes in Brine Discharges Carried out in Barranco del Toro Beach , South of Gran Canaria (Canary Islands). Desalination, 139, 277-286.

Toms, B. A. (1948). Some Observations on the Flow of Linear Polymer Solutions through Straight Tubes at Large Reynolds Numbers. Proceedings of the 1st International Congress on Rheology, 2, 135-141.

Van Driest, E. R. (1970). Turbulent Drag Reduction of Polymeric Solutions. Journal of Hydronautics, 4(3), 120-126.

Virk, P. S. (1971). An Elastic Sublayer Model for Drag Reduction by Dilute Solutions of Linear Macromolecules. Journal of Fluid Mechanics, 45(3), 417-440.

Virk, P. S. (1975, July). Drag Reduction Fundamentals. AiChE Journal, 21(4), 625-656.

Walsh, M. (1967). Theory of Drag Reduction in Dilute High-Polymer Flows. International Shipbuilding Progress, 134-139.

Wang, Y., Yu, B., Zakin, J. L., & Shi, H. (2011). Review on Drag Reduction and its Heat Transfer by Additives. Advances in Mechanical Engineering, 2011.

Wingrave, J. A., Kubena Jr., E., Douty, C. F., & Cords, D. P. (1987). New Chemical Package Produces an Improved Shale Inhibitive Water-Based Drilling Fluid System. Society of Petroleum Engineers 16687. Dallas, TX: Society of Petroleum Engineers.

Zelenev, A. S., Gilzow, G. A., & Kaufman, P. B. (2009). Fast-Inverting, Brine and Additive-Tolerant Friction Reducer for Well Stimulation. Society of Petroleum Engineers 121719. The Woodlands, TX: Society of Petroleum Engineers.

ZL Petrochemicals Co. (2012). Enhanced Oil Recovery Services. Retrieved May 1, 2014, from ZL EOR Chemicals: http://www.zlpam.com/wp-content/uploads/2011/11/About-Polyacrylamide-Fact-Sheet.pdf